Supporting Information

Ru-Catalyzed, *cis*-Selective Living Ring-Opening Metathesis Polymerization of Various Monomers, Including a Dendronized Macromonomer, and Implications to Enhanced Shear Stability

Jung-Ah Song, Gregory I. Peterson, Ki-Taek Bang, Tonia S. Ahmed, Jong-Chan Sung, Robert H. Grubbs and Tae-Lim Choi*

Department of Chemistry, Seoul National University, Seoul 08826, Korea

tlc@snu.ac.kr

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1. Materials

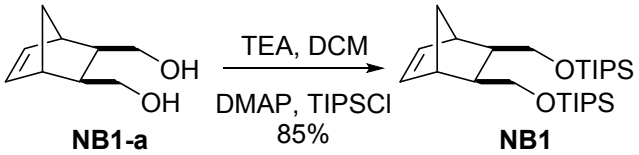
Without additional notes, all reagents which were commercially available from Sigma-Aldrich, Tokyo Chemical Industry Co. Ltd., and Alfa Aesar® were used without further purification. Solvents for monomer synthesis were commercially obtained and for polymerization, distilled THF was used. All reactions were conducted under Ar atmosphere, otherwise indicated. The Grubbs 3rd generation catalyst and Ru4 were prepared following the reported literature.[1,2] Thin-layer chromatography (TLC) was carried out on pre-coated plates (MERCK TLC silica gel 60, F254) and flash column chromatography was performed using MERCK silica gel 60 (0.040 ~ 0.063 mm). For size exclusion chromatography (SEC) analysis, BHT-contained (104 ppm) SEC grade THF was purchased from J. T. Baker®.

2. General Information

NMR spectra for monomers were recorded by Varian/Oxford As-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer and Agilent 400-MR (400 MHz for ^{1}H and 100 MHz for ^{13}C). NMR spectra for polymers were recorded by AVANCE III HD (850 MHz for ^{1}H, and 213 MHz for ^{13}C) in National Center for Inter-University Research Facilities (NCIRF). Size exclusion chromatography (SEC) analyses were carried out with the Waters system (515 pump, 2707 autosampler with a loop volume of 100μL), Wyatt OptiLab T-rEx refractive index detector and DAWN-HELEOS 8+ multi-angle laser light scatter. The flow rate was 1.0 mL/min and temperature of the column was maintained at 35 °C. Samples were diluted in 0.001-0.005 wt% by THF and filtered through a 0.20 μm PTFE filter before using. High-resolution mass spectroscopy (HRMS) analyses were performed by JMS-700 MStation Mass Spectrometer (Japan) in the National Center for Inter-University Research Facility and by the ultra HR-ESI Q-TOF mass spectrometer (Bruker, Germany) in the Sogang Center for Research Facilities.

3. Experimental Procedure for Small Molecule Synthesis

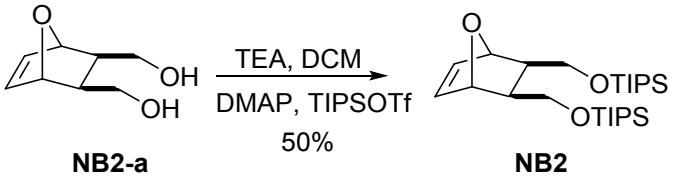
TD1[3], **TD2**[4], **NB3**[5] and **NB4**[6] were synthesized according to the literature and their spectroscopic data were reported in the same literature.



NB1-a **NB1**

Scheme S1. Synthesis of NB1

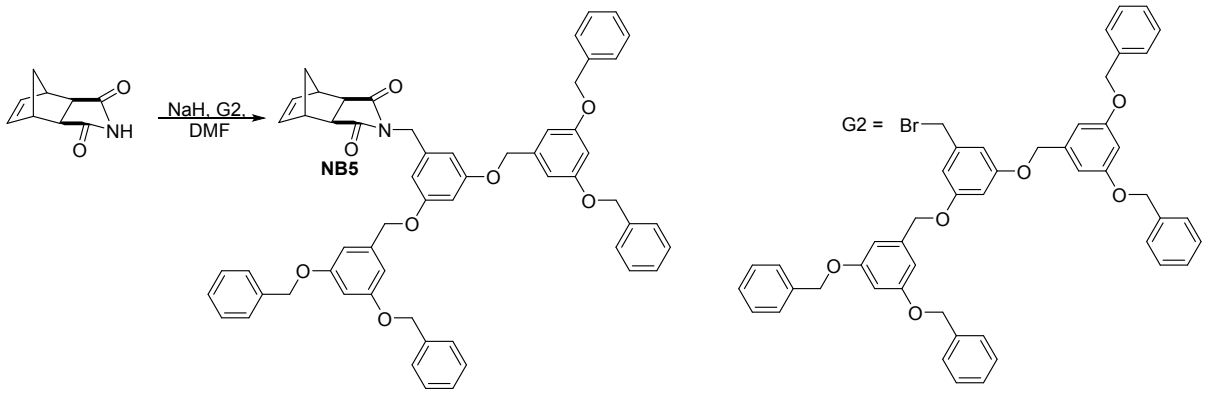
NB1: **NB1-a** (0.50 g, 0.0032 mol) was dissolved in DCM. To this solution, TEA (1.1 ml, 0.008 mol), DMAP (18.3 mg, 0.00015 mol) and TIPSCl (1.5 ml, 0.007 mol) were added. After The product was purified by column chromatography (EtOAc:Hexane=1:15) to afford the product **NB1** (1.27 g, 0.0027 mol, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (t, *J* = 1.7 Hz, 2H, CHC<u>H</u>C<u>H</u>CH), 3.92 (dt, *J* = 12.9, 6.5 Hz, 2H, CHC<u>H$_2$</u>OTIPS), 3.64 – 3.55 (m, 2H, CHC<u>H$_2$</u>OTIPS), 2.83 – 2.74 (m, 2H, C<u>H</u>CHCHC<u>H</u>), 1.70 – 1.62 (m, 2H, CH$_2$C<u>H</u>C<u>H</u>CH$_2$), 1.52 (d, *J* = 8.8 Hz, 1H, CHC<u>H$_2$</u>), 1.26 – 1.20 (m, 1H, CHC<u>H$_2$</u>), 1.08 – 1.03 (m, 42H, OTIPS), ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.46, 64.50, 44.48, 43.30, 42.51, 18.04, 11.96. HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{27}H_{54}O_2Si_2$, 489.3560, found, 489.3556.



NB2-a **NB2**

Scheme S2. Synthesis of NB2

NB2: **NB2-a** (0.5 g, 0.0032 mol) was dissolved in DCM. To this solution, TEA (1.1 ml, 0.008 mol), DMAP (18.3 mg, 0.00015 mol) and TIPSOTf (1.9 ml, 0.007 mol) were added. After The product was purified by column chromatography (EtOAc:Hexane=1:10) to afford the product **NB2** (0.75 g, 0.0016 mol, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 2H, CHC<u>H</u>C<u>H</u>CH), 4.87 (s, 2H, C<u>H</u>OC<u>H</u>), 3.92 – 3.83 (m, 2H, CHC<u>H$_2$</u>OTIPS), 3.69 – 3.60 (m, 1H, CHC<u>H$_2$</u>OTIPS), 1.85 – 1.77 (m, 2H, CH$_2$C<u>H</u>C<u>H</u>CH$_2$), 1.14 – 1.01 (m, 42H, OTIPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.52, 80.41, 80.36, 62.73, 42.64, 18.00, 11.92. HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{26}H_{52}O_3Si_2$, 491.3353, found, 491.3349.



Scheme S3. Synthesis of NB5

NB5: NB5 was prepared using a modified literature procedure.[6] To a stirred solution of **NB5-a** (494mg, 3 mmol) in DMF (20mL), sodium hydride (60wt% dispersion in mineral oil, 121mg, 3 mmol) was added slowly at 0°C and stirred for 20min. To a reaction mixture, G2 (1.63g, 2 mmol) was added and stirred for 4h at RT. The reaction was quenched by water at 0°C. After extraction with dichloromethane twice, the combined organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. After, the product was purified by column chromatography (DCM to DCM:EtOAC = 10:1) to afford the product **NB5** (1.42 g, 1.6 mol, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 28.0, 16.3, 7.2 Hz, 20H, Ph), 6.68 (d, *J* = 2.1 Hz, 4H, CC<u>H</u>CCH$_2$O), 6.61 (d, *J* = 2.1 Hz, 2H, OCC<u>H</u>CO), 6.57 (t, *J* = 2.1 Hz, 2H, NCH$_2$CC<u>H</u>), 6.50 (t, *J* = 2.1 Hz, 1H, OCC<u>H</u>CO), 6.24 (s, 2H, CHC<u>H</u>C<u>H</u>CH), 5.04 (s, 8H, OC<u>H$_2$</u>Ph), 4.95 (s, 4H, OC<u>H$_2$</u>), 4.55 (s, 2H, N<u>H$_2$</u>), 3.23 (s, 2H, CHC<u>H</u>CH), 2.66 (s, 2H, CHC<u>H</u>C), 1.40 (d, *J* = 9.9 Hz, 1H, CHC<u>H$_2$</u>), 1.08 (d, *J* = 9.8 Hz, 1H, CHC<u>H$_2$</u>). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.54, 177.54, 160.16, 160.16, 159.93, 159.93, 139.22, 138.02, 137.87, 136.82, 128.54, 127.95, 127.52, 107.83, 106.39, 101.70, 70.12, 69.92, 47.79, 45.29, 42.70, 42.35. HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{58}H_{51}NO_8$, 912.3513, found, 912.3504.

4. General Procedure for Polymerization

A 4-mL sized screw-cap vial with septum was flame dried and charged with monomer and a magnetic bar. Monomer was weighed in the vial and the vial was purged with argon three times. Then, degassed anhydrous THF was added to the solution. After the Ar-purged catalyst (**Ru4**, **GIII** or 1st generation Grubbs catalyst) in another 4-mL vial was dissolved in THF (in case of the reaction that **ClPy** or **Py** is needed, **ClPy** was added to the **Ru4** solution), the solution was rapidly injected to the monomer solution at rt or 55 °C under vigorous stirring. The reaction was quenched by excess ethyl vinyl ether after desired reaction time, and concentrated by evaporation. The polymer was purified by precipitation in methanol (except **PNB5**) or diethyl ether (**PNB5**) at rt. Obtained polymer was filtered and dried in vacuo. Remaining small amount of crude mixture (<10%) was used for calculating the monomer conversion by ^{1}H NMR.

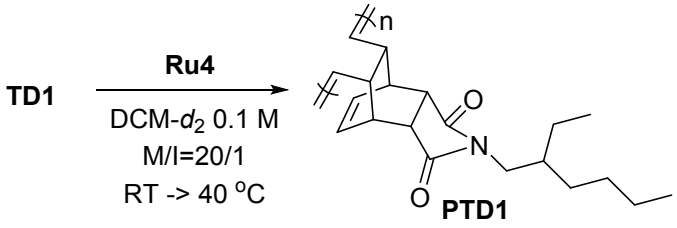
5. Procedure for Block Copolymerization.

Procedures was same with the general polymerization. Conversion of the first monomer was monitored by TLC, then the second monomer was added.

6. Mechanistic Studies

① ROMP of TD1 using Ru4 in NMR tube

Ru4 (2.1 mg, 0.0025 mmol) and hexamethyldisilane (5 µl) were dissolved in DCM-d_2 (4.5 ml). Initial benzylidene was measured by integral ratio of **Ru4** to hexamethyldisilane in ^{1}H NMR spectrum. **TD1** (15.7 mg, 0.05 mmol) DCM-d_2 (50 µl) solution was added to the **Ru4** solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was monitored by ^{1}H NMR.



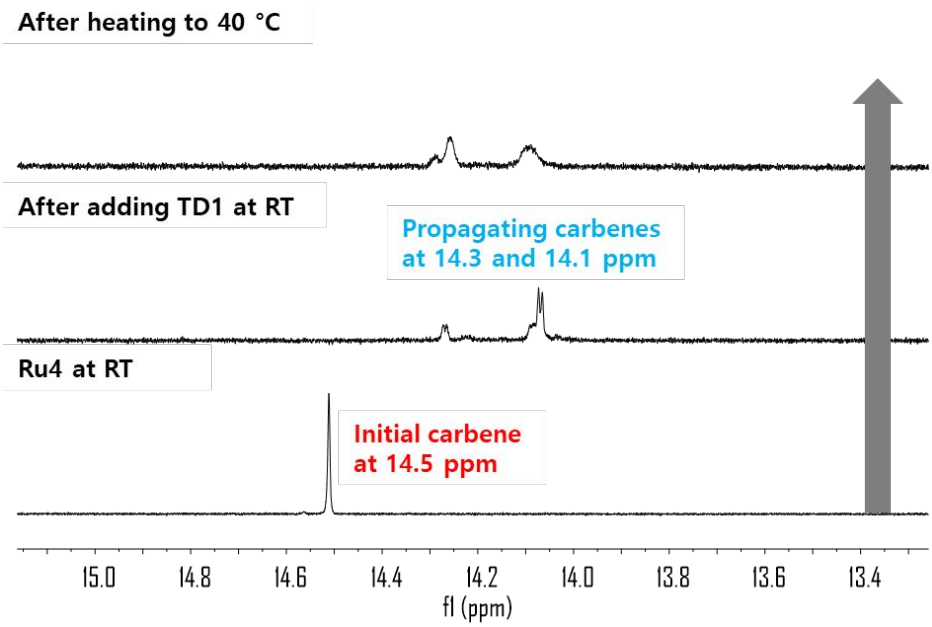


Figure S1. ^{1}H NMR spectra of carbenes upon addition of TD1

While heating, we also monitored the consumption of monomer over time. To check the livingness (reaction order), we plotted $\ln(M/M_0)$ vs time and it showed linear relationship, which means ROMP of **TD1** using **Ru4** is a first-order reaction.

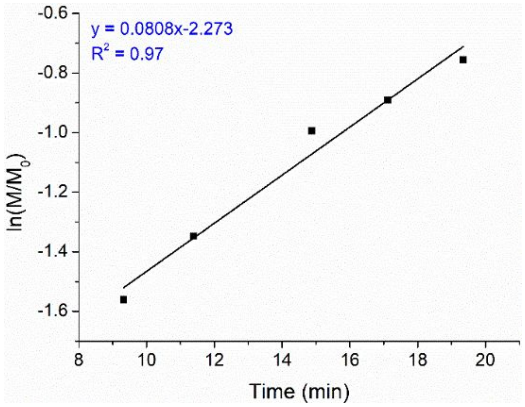


Figure S2. Plot of $\ln(M/M_0)$ vs time.

② Determination of k_i/k_p of ROMP of NB2

The propagating carbene was monitored by ^{1}H NMR. k_i/k_p was calculated using the following equation.[8]

$$M-M_0 = (1-1/r)(I-I_0) + rI_0\ln(I/I_0) \text{ if } I \neq 0$$

where $r = k_i/k_p$, M = concentration of monomer, M_0 = initial concentration of monomer, I = concentration of initiator, and I_0 = initial concentration of initiator. By measuring the amount of remaining initiator (I), r can be determined.

Two different THF-d_8 (0.45 ml) solutions of **Ru4** (2.1 mg, 0.0025 mmol) and hexamethyldisilane (5 µl) were prepared. 1 µl of **ClPy** (2.4 µl (0.0025 mmol) in 7.6 µl THF-d_8) solution was added to one **Ru4** solution only. Other steps were same but conducted, respectively. Initial benzylidene was measured by integral ratio of **Ru4** to hexamethyldisilane in ^{1}H NMR spectrum. **NB2** (23.44 mg, 0.05 mmol) THF-d_8 (50 µl) solution was added to the **Ru4** solution and mixed by shaking NMR tube for 10 sec.

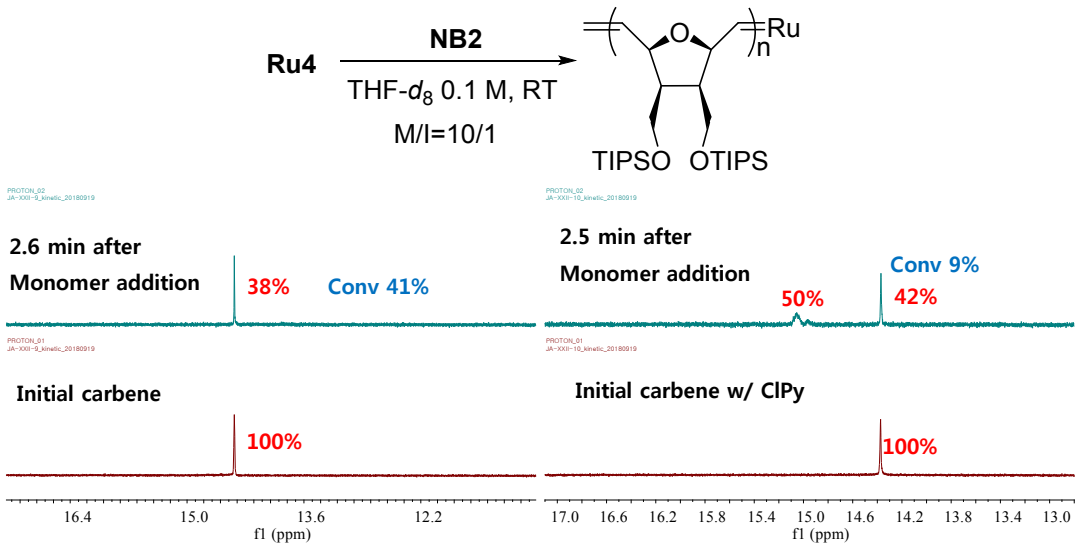


Figure S3. ^{1}H NMR spectra of carbenes upon addition of NB2

7. GPC Traces of PTDs and PNBs

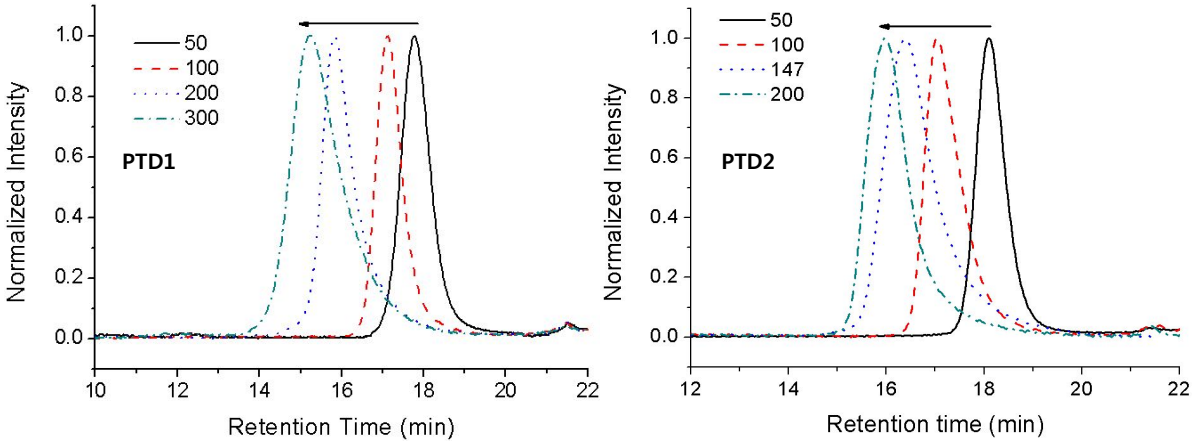
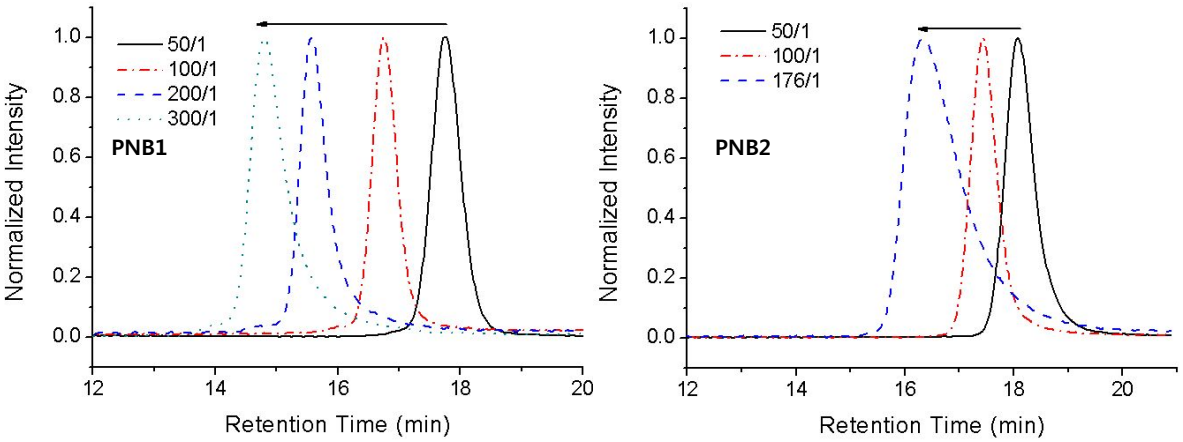


Figure S4. Molecular weight control of PTD



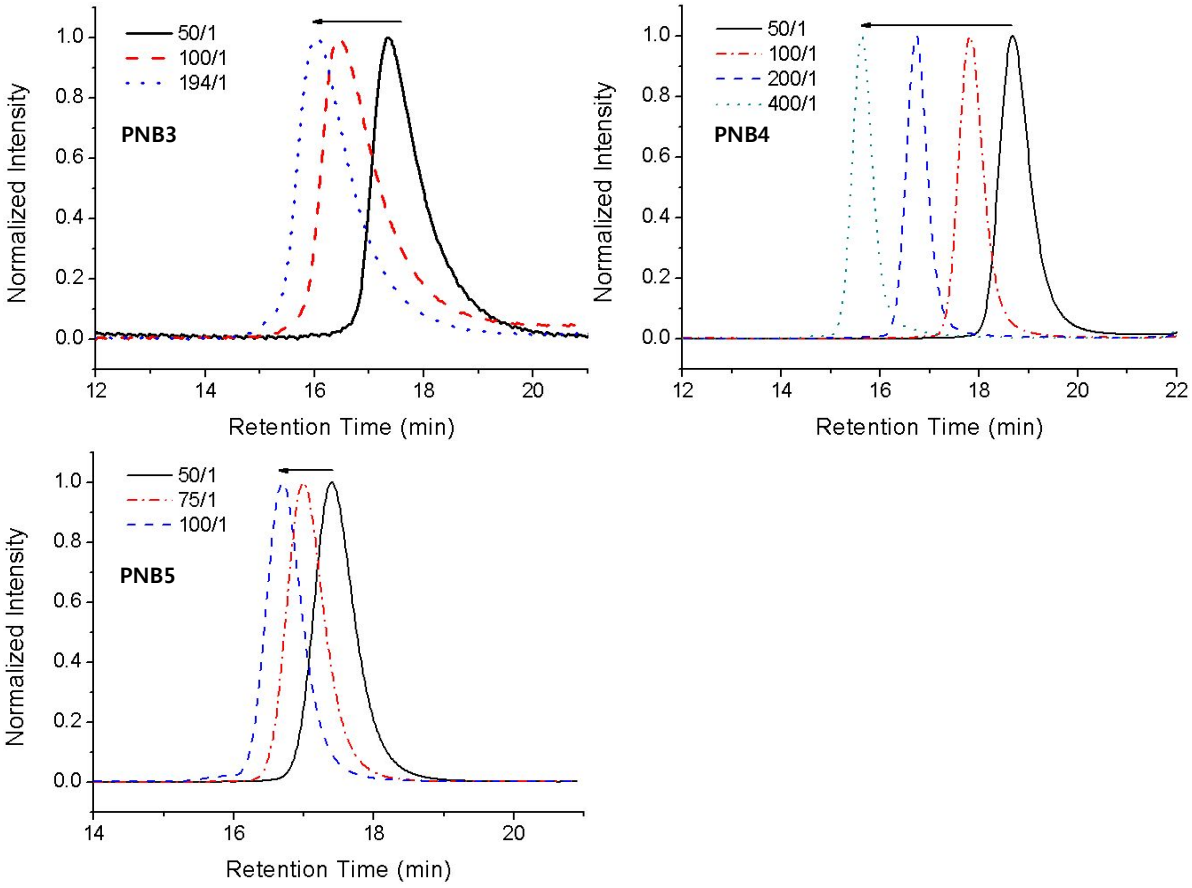


Figure S5. Molecular weight control of PNB

8. Polymer Degradation Studies and Analysis

For sonication studies, we used a 20 kHz Sonics VCX-500 series sonication probe with an extender tip (1.25 cm tip diameter), calibrated according to literature procedures.[9] Degradation studies were conducted as previously described.[10,11] In short, an Ar-purged solution of polymer in inhibitor-free, HPLC-grade THF (15 mg of polymer at 1 mg/mL concentration) was prepared in a sealed Suslick flask under Ar atmosphere. The Suslick flask was submerged in a cold bath (maintained at -10 ˚ C by a recirculating chiller) and the polymer solutions was sonicated at 16.9 W/cm^2 using a pulse sequence of 1 s "on", 4 s "off". Aliquots were withdrawn periodically and analyzed by SEC. Persistence length values were calculated from M_w and R_{gz} data, obtained by SEC MALS, using the Benoit-Doty law.[12,13] First order rate constants were determined using methods previously described.[10] In short, the decrease in parent polymer concentration (with increasing sonication time) was monitored by following the decrease in SEC RI signal at the retention time which corresponds to the parent polymer peak maximum value. Rate constants were determined from the linear slope of plots of Ln (RI signal) versus sonication time.

9. ^{1}H and ^{13}C NMR characterization of polymers

PTD1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (br, m, 2H), 5.12 (br, m, 2H), 3.09 (br, m, 8H), 1.60 (br, s, 1H), 1.21 (br, s, *J* = 28.1 Hz, 8H), 0.86 (br, s, 6H). ^{13}C NMR (214 MHz, $CDCl_3$) δ 178.54, 178.34, 132.20, 131.15, 43.92, 42.57, 40.64, 38.69, 37.56, 37.40, 30.41, 28.55, 23.64, 23.11, 14.18, 10.33.

PTD2: ^{1}H NMR (850 MHz, $CDCl_3$) δ 7.21-6.91 (m, 10H), 6.14-5.87 (br, m, 2H), 5.50 – 4.87 (m, 2H), 4.36 – 4.08 (m, 4H), 3.35 – 1.99 (m, 10H). ^{13}C NMR (214 MHz, $CDCl_3$) δ 139.49, 138.96, 133.58, 132.39, 128.33, 128.23, 127.73, 127.48, 127.25, 127.15, 73.05, 72.47, 71.60, 70.42, 42.66, 42.12, 41.74, 41.46, 40.55, 39.75.

PNB1: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.18 (s, 1H), 3.71 (d, J = 53.6 Hz, 2H), 2.67 (s, 1H), 2.27 – 2.09 (m, 1H), 2.00 (s, 1H), 1.05 (s, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.63, 134.12, 63.31, 63.04, 50.96, 50.59, 41.91, 41.66, 41.43, 41.07, 40.87, 40.24, 39.86, 39.48,

39.30, 38.97, 38.84, 18.28, 12.18, 12.13.

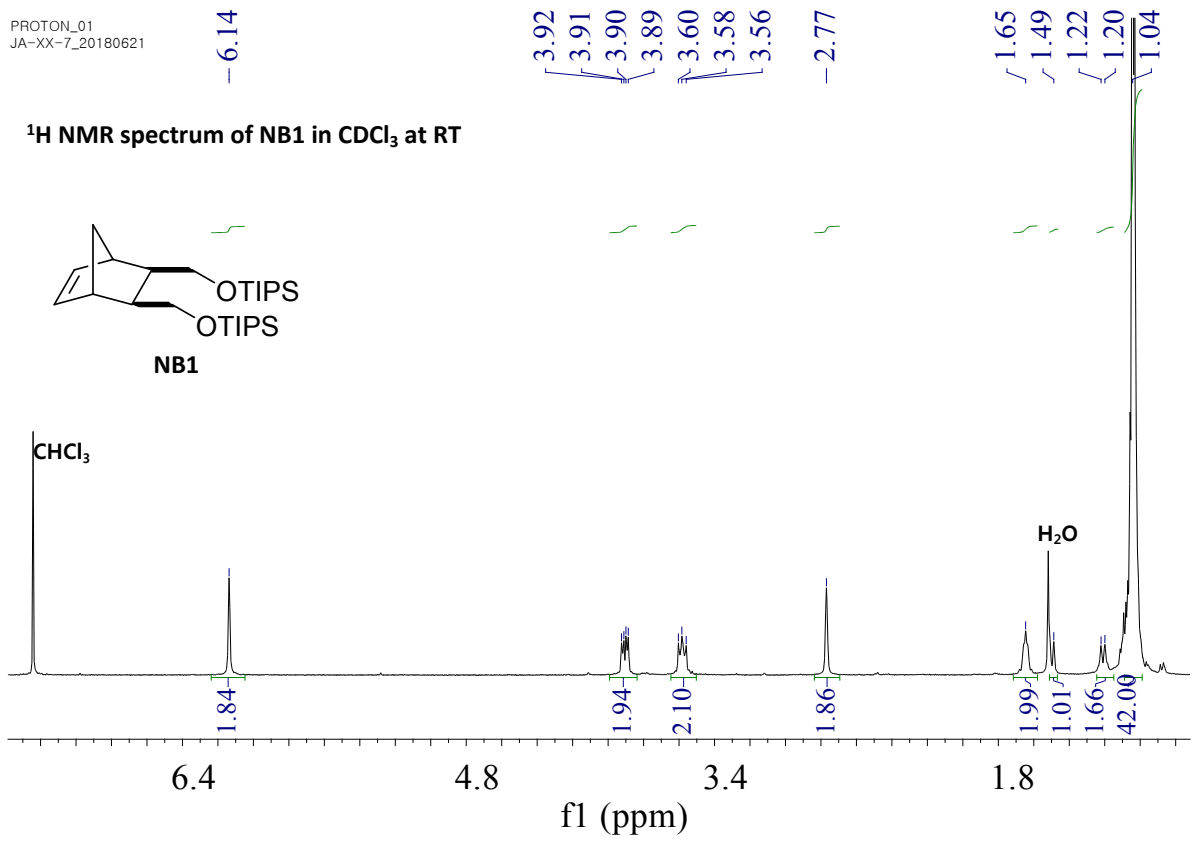
PNB2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (br, s, 2H), 4.64 (br, s, 2H), 3.83 (br, s, 2H), 3.66 (br, s, 2H), 2.25 (br, s, 2H), 1.05 (br, m ,42H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.07, 77.23, 61.36, 50.55, 18.24, 18.22, 12.13.

PNB3: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.38 – 5.28 (m, 1H), 5.18 (s, 1H), 3.69 (m, *J* = 2.0 Hz, 2H), 3.60 (m, *J* = 12.9 Hz, 4H), 3.36-3.02 (br, m, 3H), 2.96 (s, 1H), 2.15 – 1.75 (m, 1H), 1.52 – 1.21 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.36, 174.22, 173.38, 173.07, 133.38, 133.10, 130.49, 130.21, 130.00, 53.08, 52.97, 52.60, 52.34, 52.10, 51.74, 42.05, 41.71, 40.84, 40.68, 39.87, 39.46, 38.74.

PNB4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (br, m, 2H), 3.30 (br, s, 3H), 3.14 (br, m, 2H), 2.95 (br, m, 1H), 2.35-1.95 (br, m, 1H), 1.69 (br, s, 1H), 1.56 (br, s, 1H), 1.22 (br, m, 8H), 0.83 (br, m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.42, 133.39, 52.98, 52.79, 52.48, 52.28, 42.61, 41.74, 41.50, 37.35, 30.55, 30.50, 30.47, 28.51, 28.48, 23.76, 23.71, 23.06, 23.04, 14.11, 10.35, 10.29.

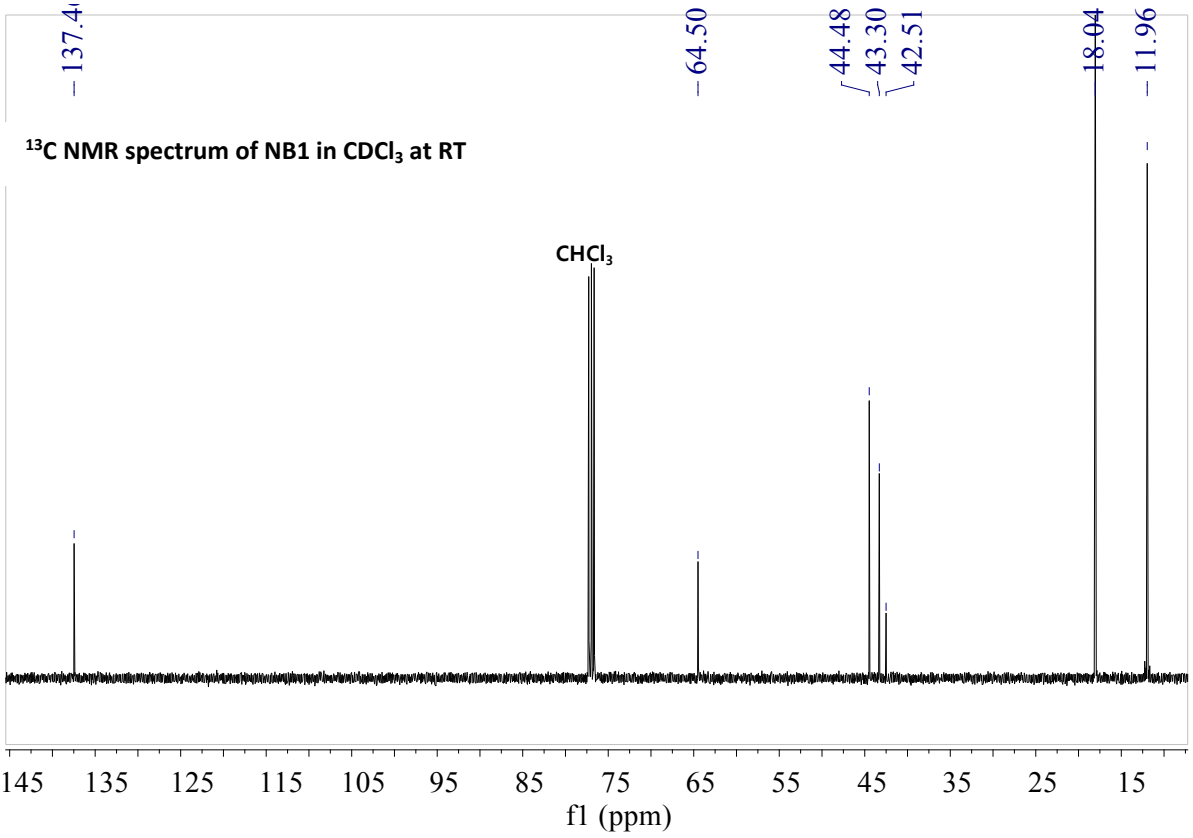
PNB5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 20H), 6.62 – 6.33 (m, 9H), 5.40 (br, s, 2H), 4.99 – 4.67 (m, 12H), 4.45 (br, s, 2H), 3.42 – 2.82 (m, 4H), 2.19 (d, *J* = 46.9 Hz, 1H), 1.54 (br, s, 1H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 177.83, 160.05, 159.91, 139.27, 138.36, 136.89, 133.71, 133.10, 128.55, 127.93, 127.61, 107.27, 106.41, 101.61, 69.95, 69.78, 53.10, 52.56, 42.32, 41.58.

10. ^{1}H and ^{13}C NMR spectra of monomers

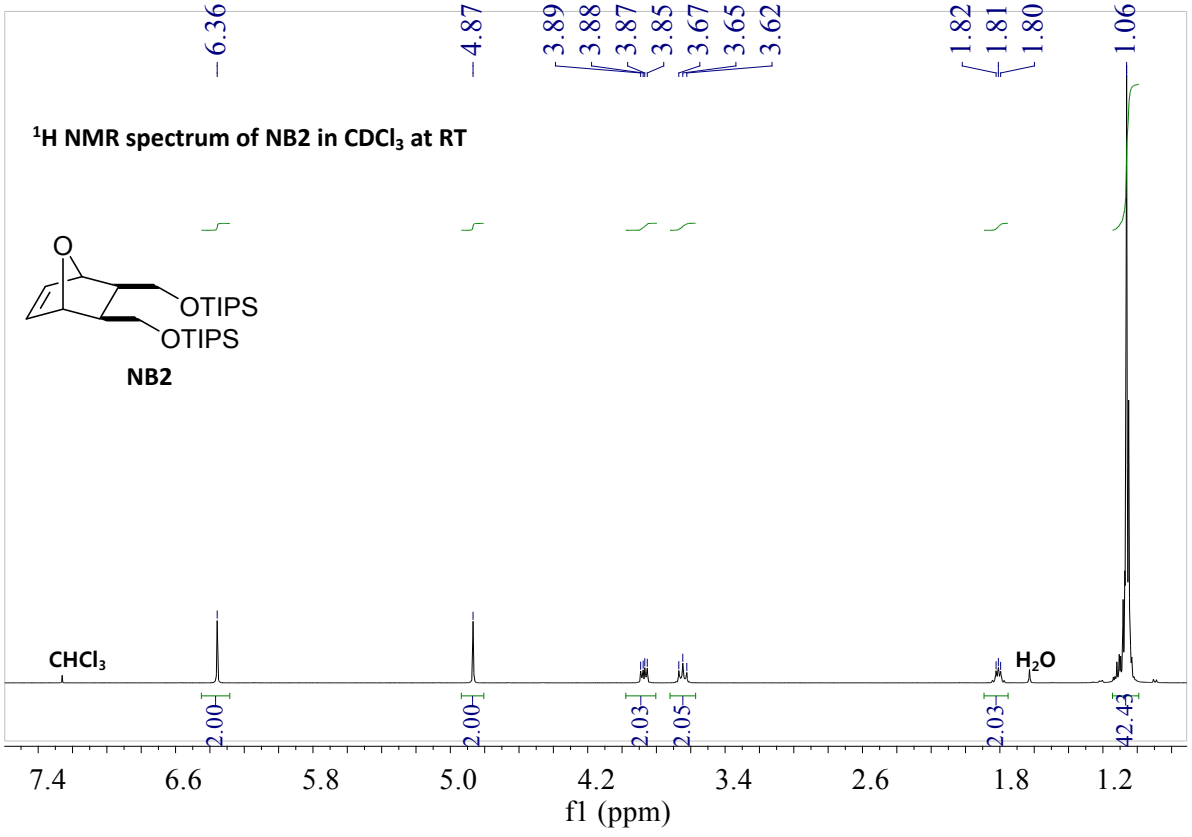


^{1}H NMR spectrum of NB1 in $CDCl_3$ at RT

NB1

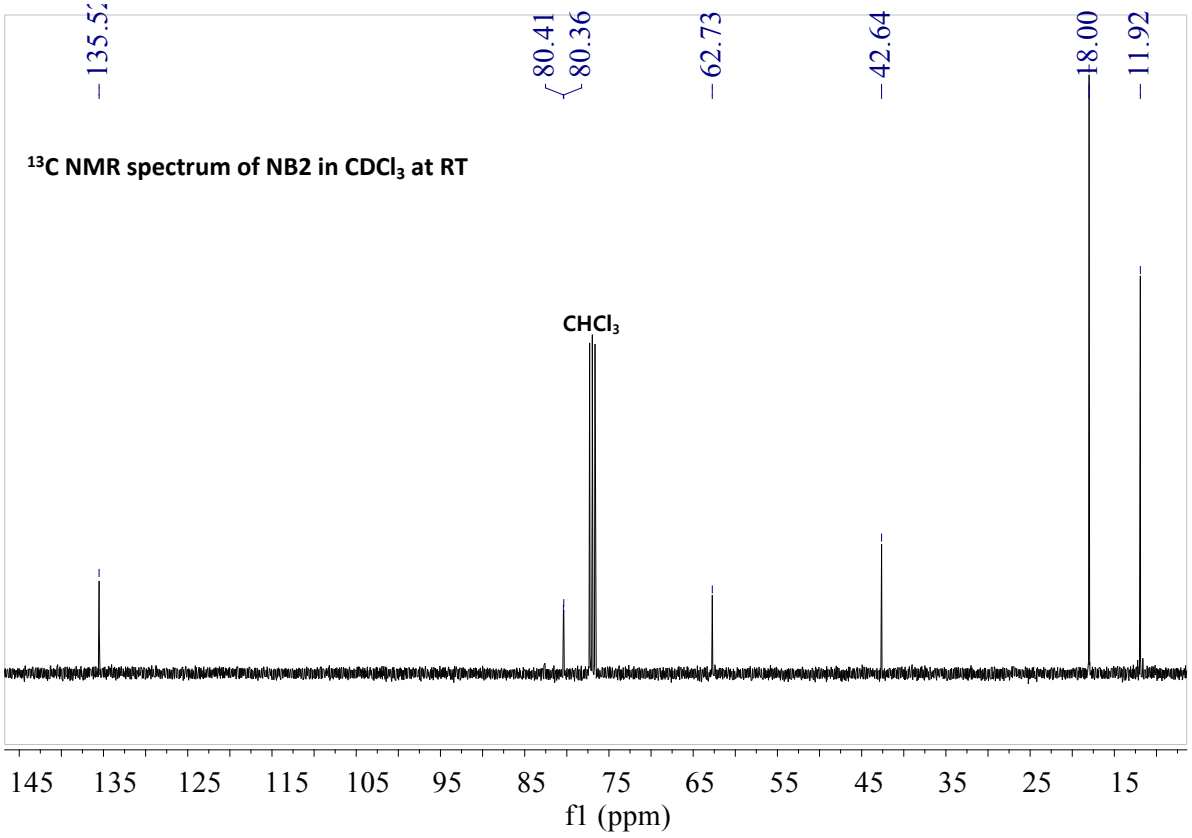


^{13}C NMR spectrum of NB1 in $CDCl_3$ at RT

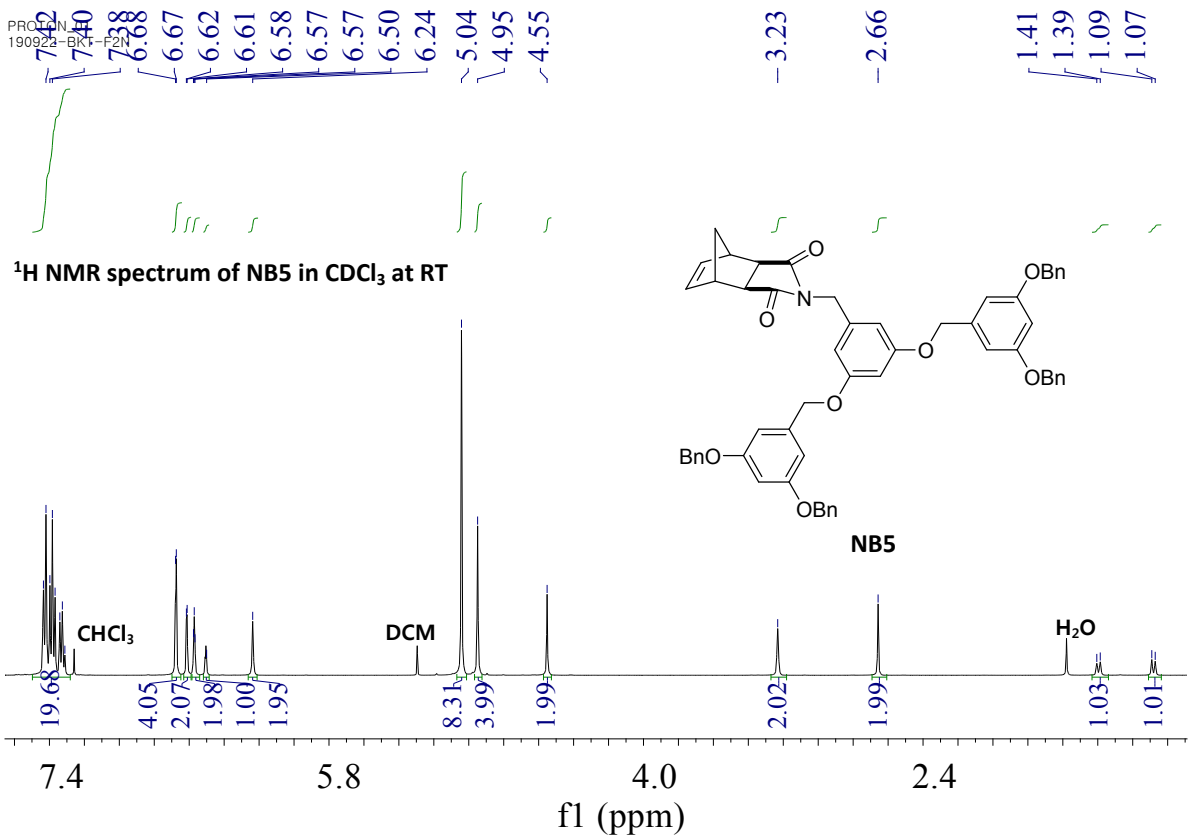


^{1}H NMR spectrum of NB2 in $CDCl_3$ at RT

NB2



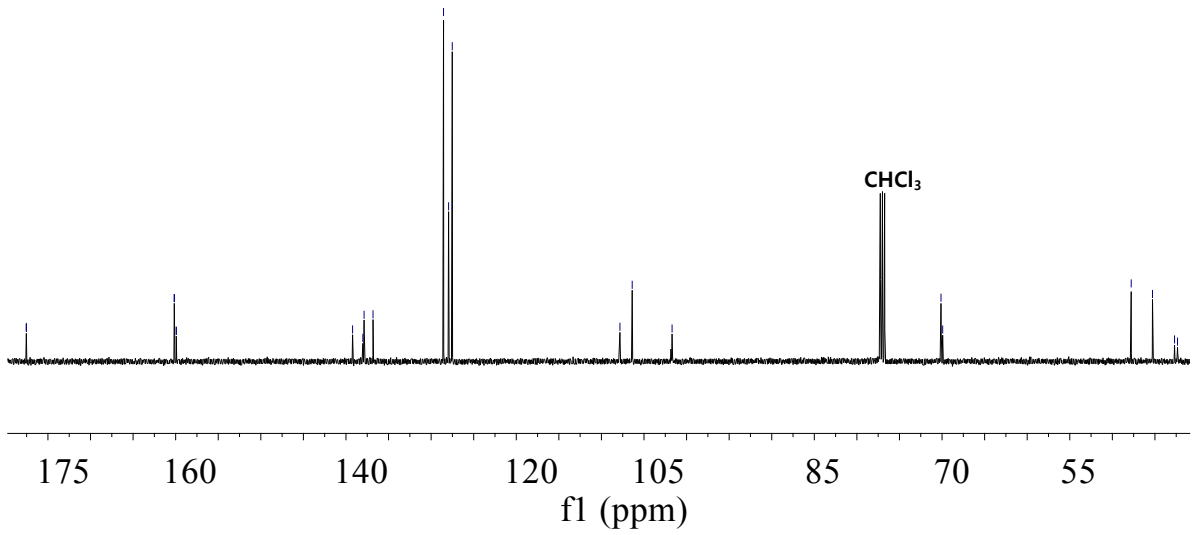
^{13}C NMR spectrum of NB2 in $CDCl_3$ at RT



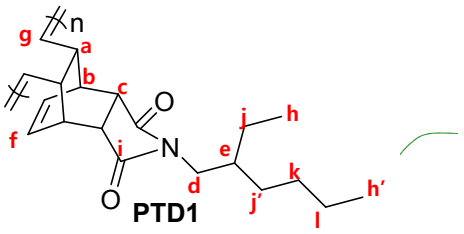
^{1}H NMR spectrum of NB5 in $CDCl_3$ at RT

NB5

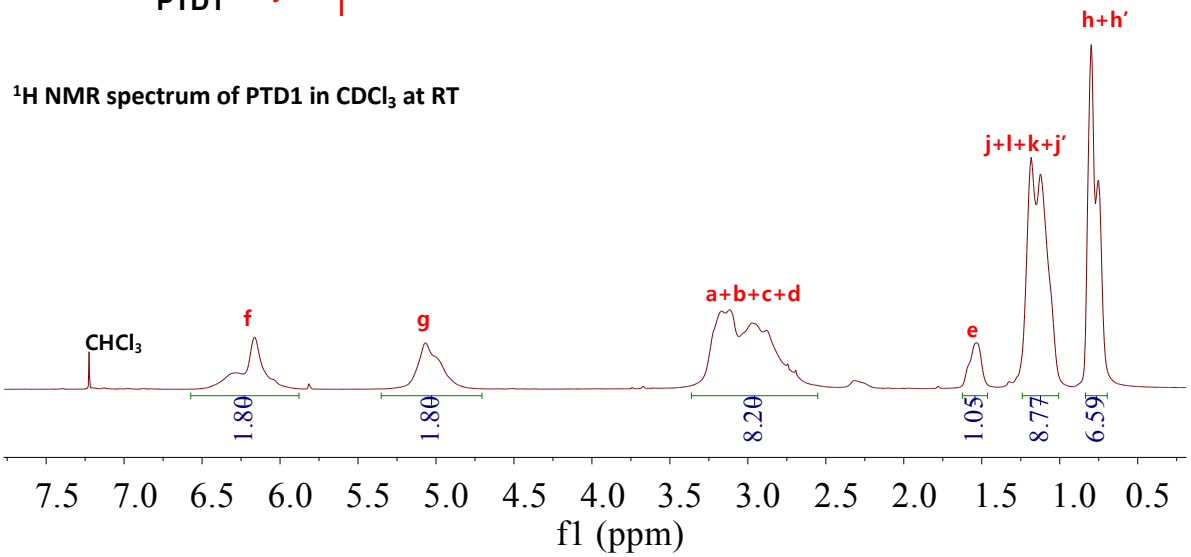
^{13}C NMR spectrum of NB5 in $CDCl_3$ at RT



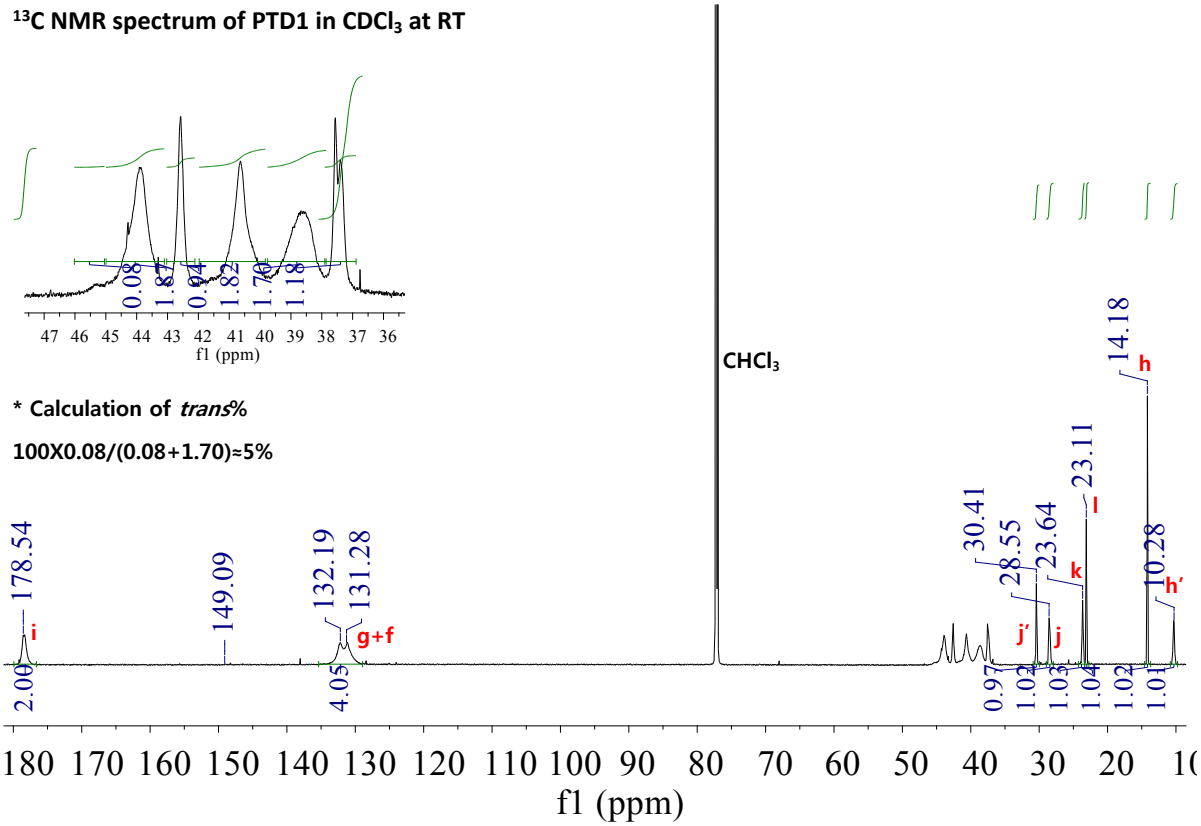
11. ^{1}H and ^{13}C NMR spectra of polymers



^{1}H NMR spectrum of PTD1 in $CDCl_3$ at RT



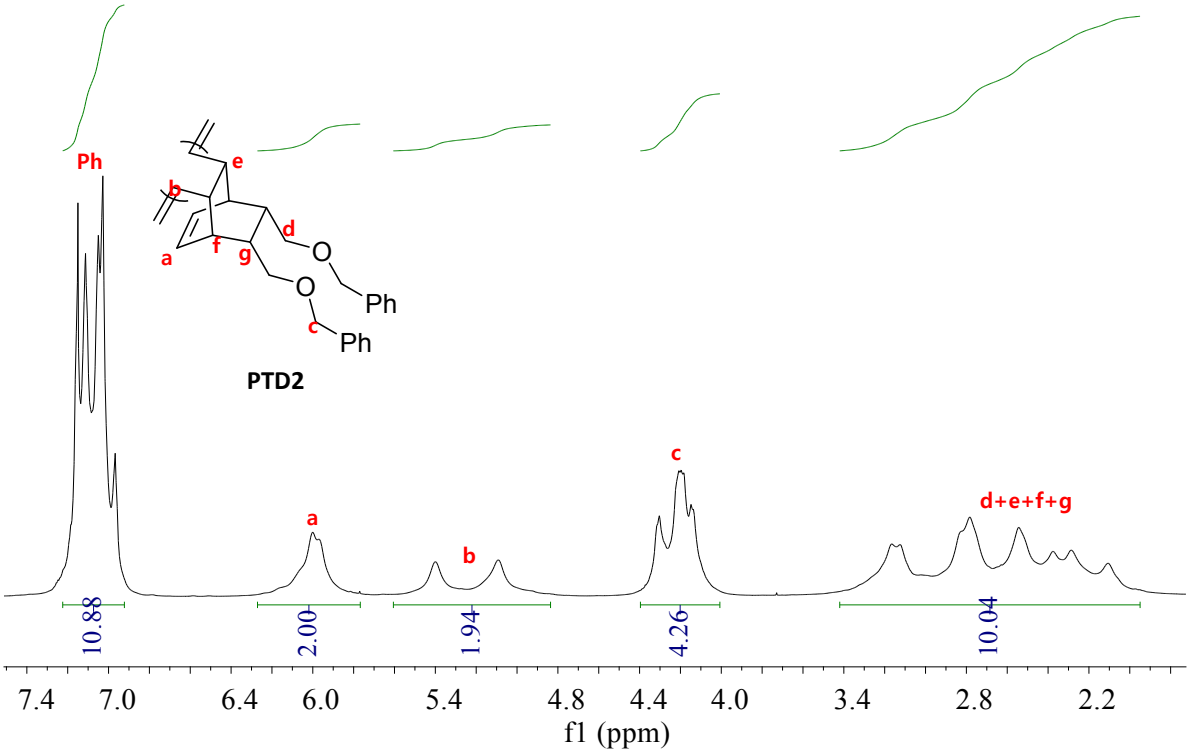
^{13}C NMR spectrum of PTD1 in $CDCl_3$ at RT



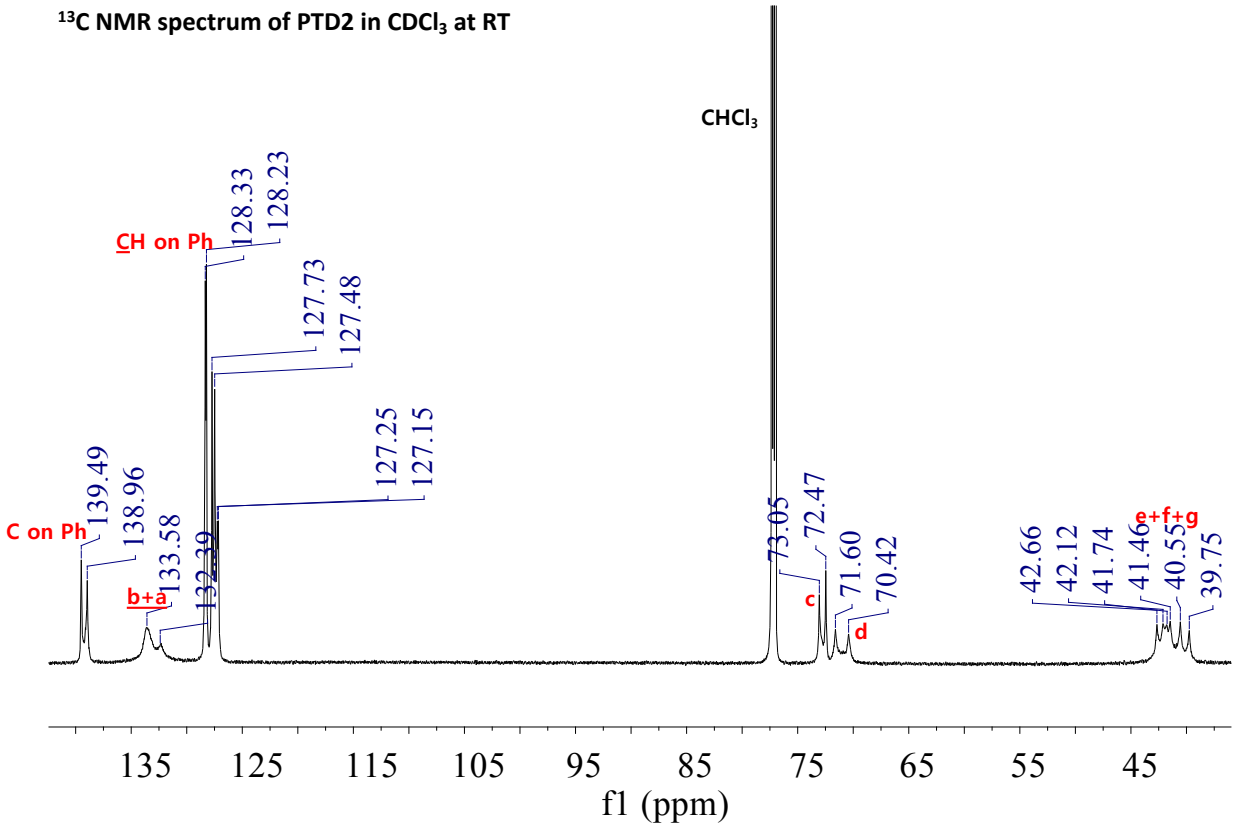
*** Calculation of *trans*%**

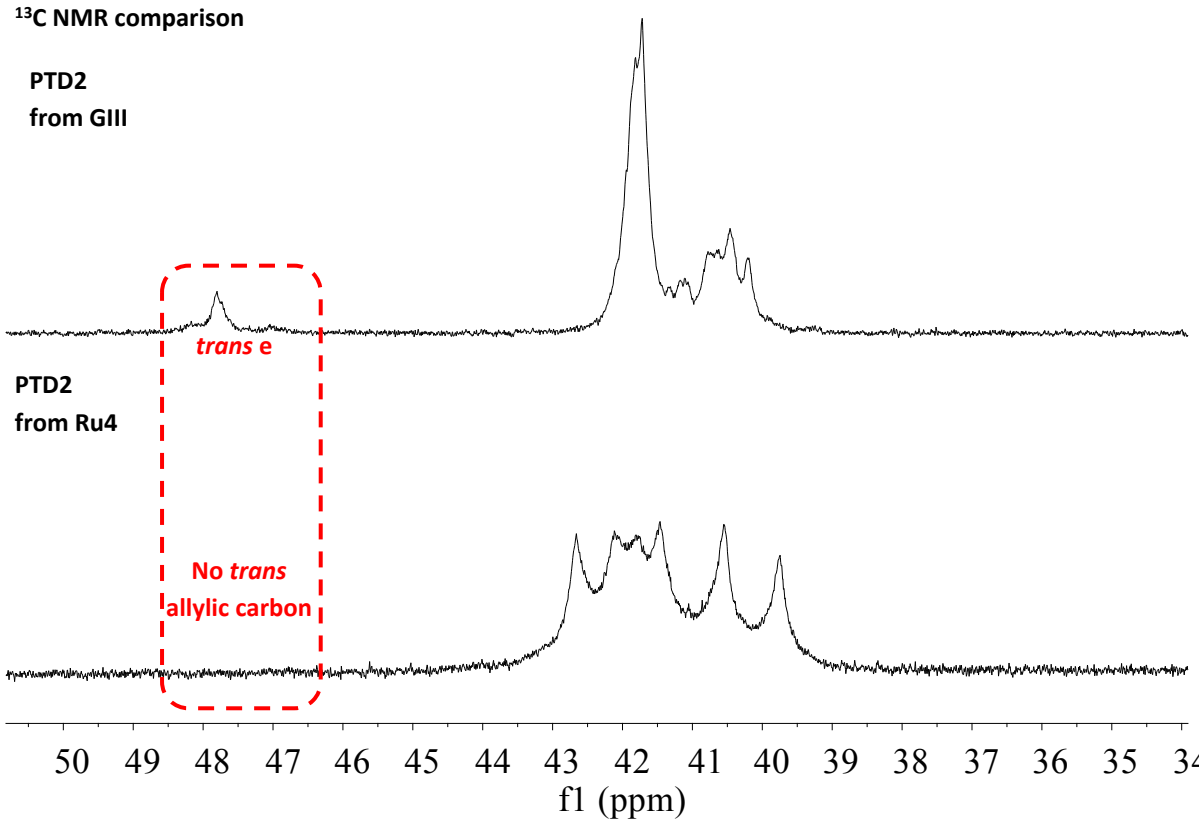
100X0.08/(0.08+1.70)≈5%

^{1}H NMR spectrum of PTD2 in $CDCl_3$ at RT

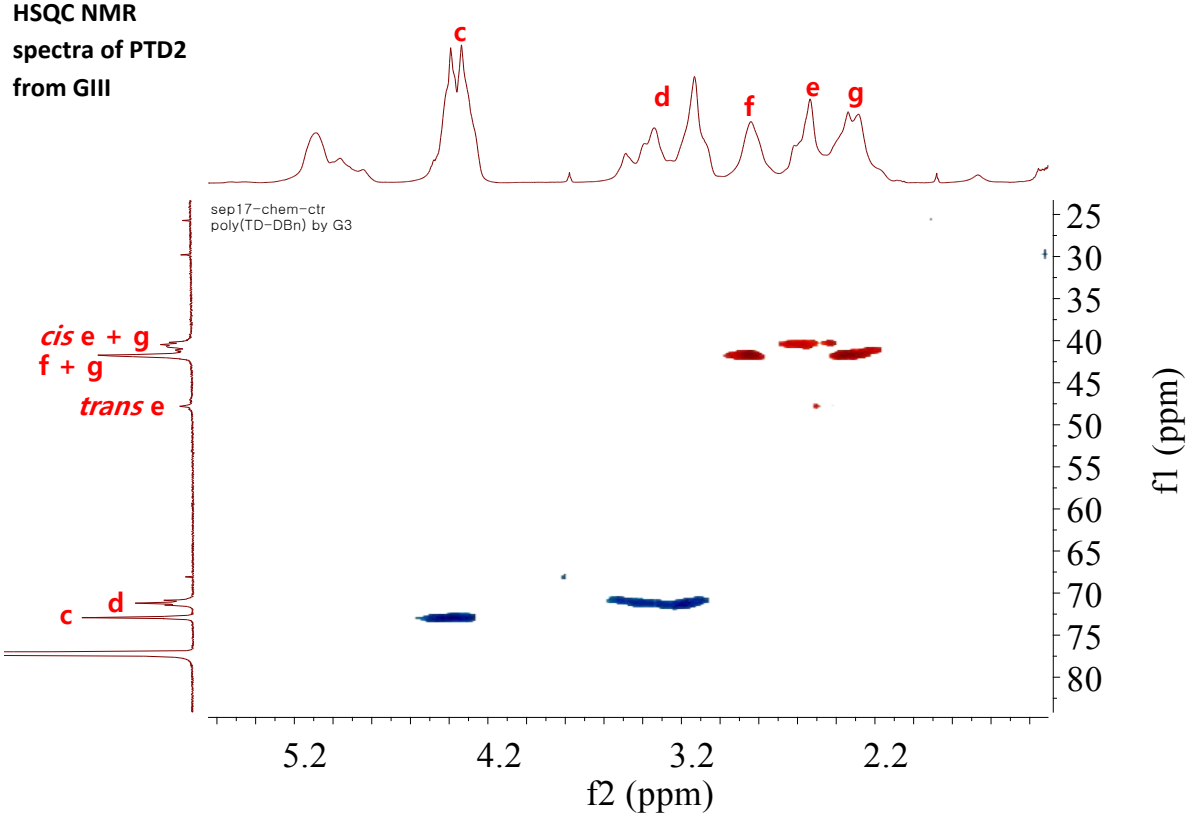


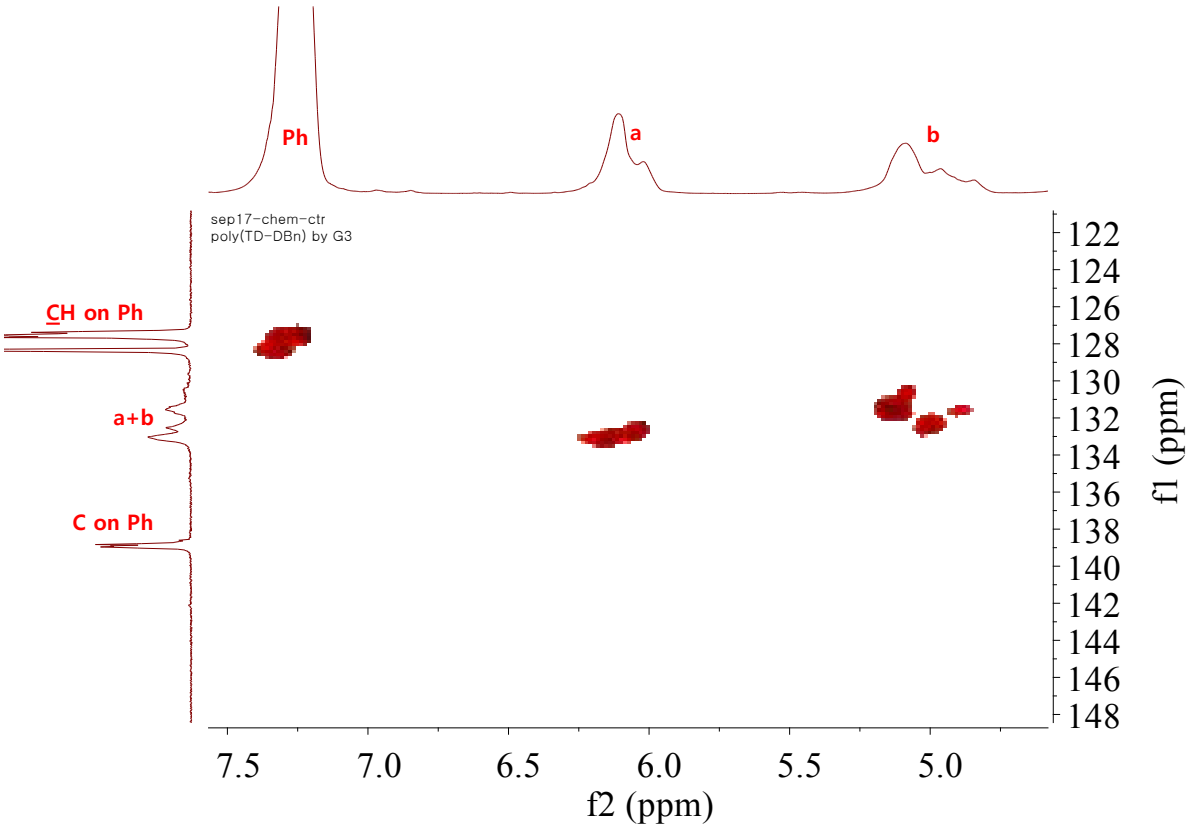
^{13}C NMR spectrum of PTD2 in $CDCl_3$ at RT



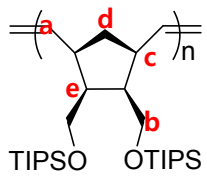

13C NMR comparison
PTD2
from GIII
trans e
PTD2
from Ru4
No trans
allylic carbon
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35
f1 (ppm)

HSQC NMR spectra of PTD2 from GIII





SJA0914
Poly(NB-OTIPS)
1H NMR
CDCl3

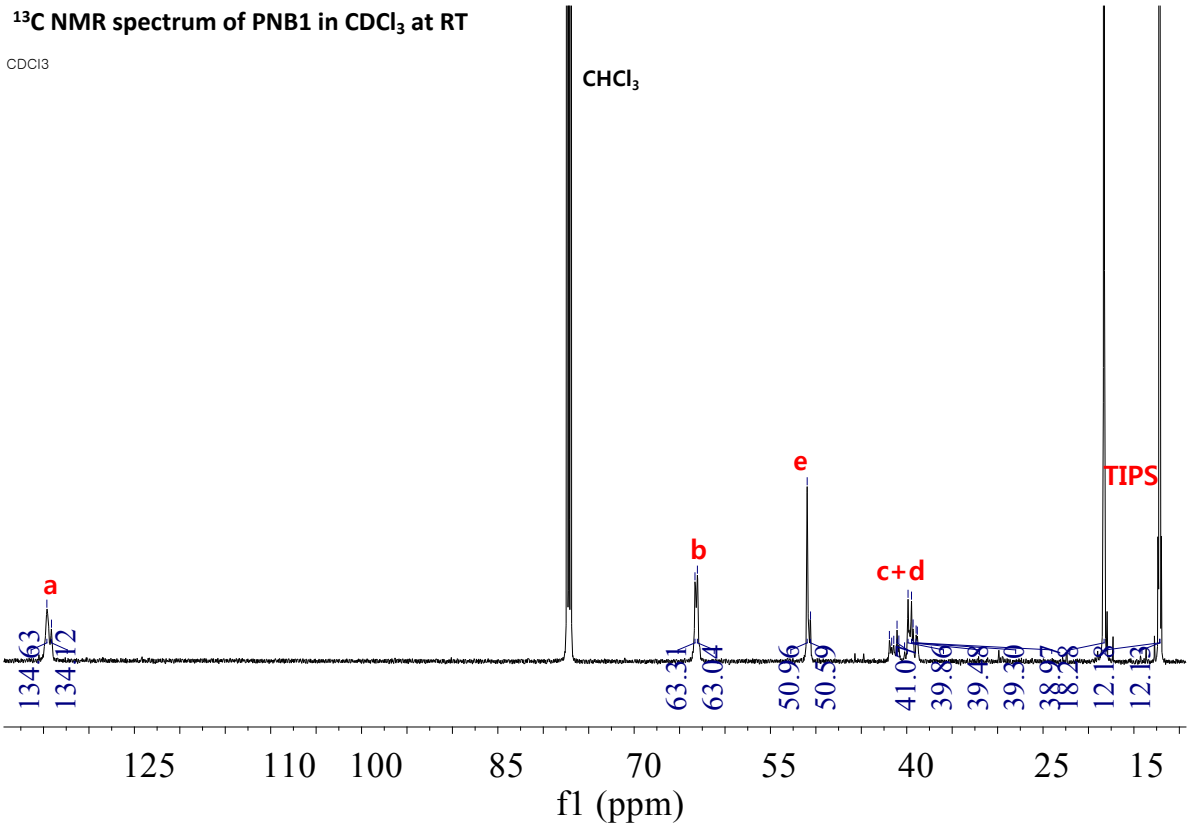


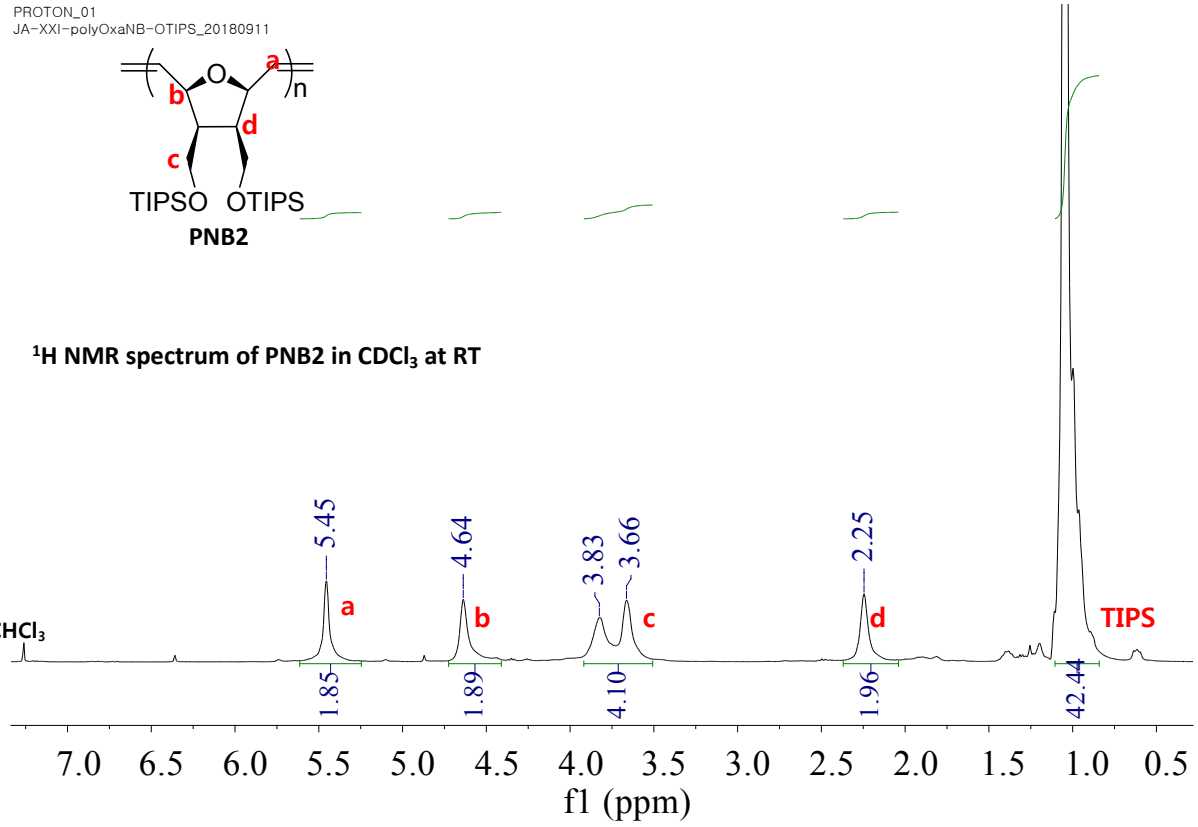
PNB1

^{1}H NMR spectrum of PNB1 in $CDCl_3$ at RT

^{13}C NMR spectrum of PNB1 in $CDCl_3$ at RT

CDCl3



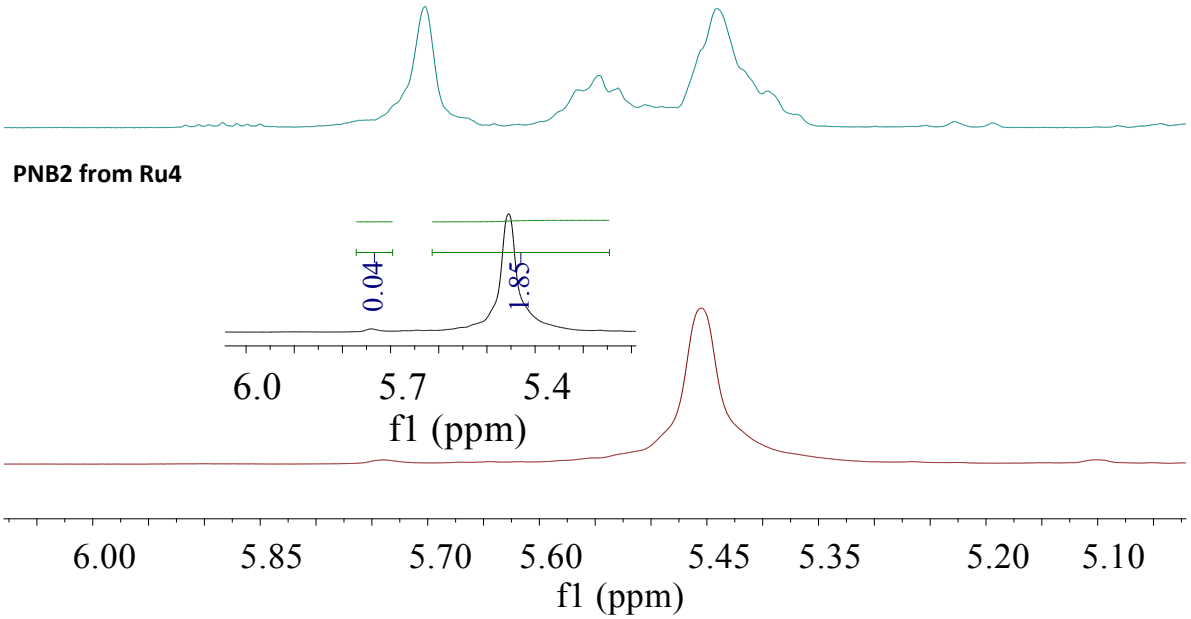


^{1}H NMR spectrum of PNB2 in $CDCl_3$ at RT

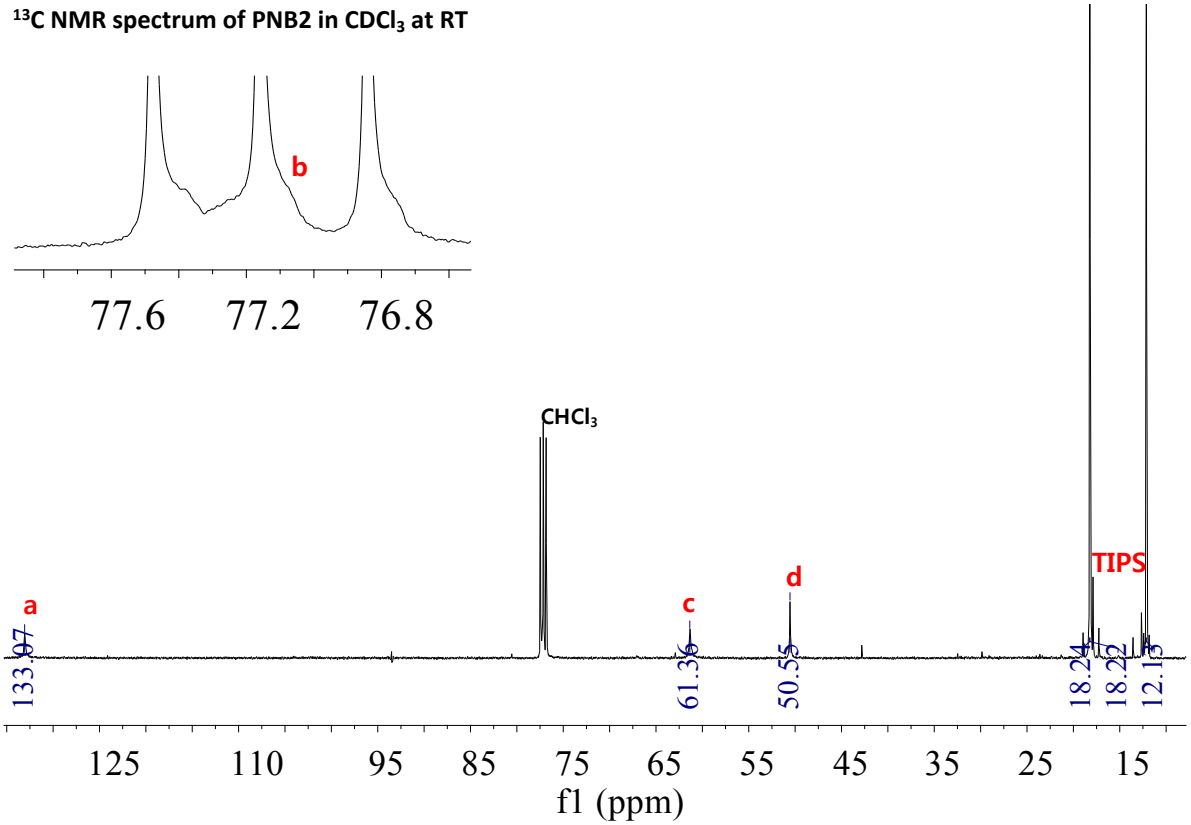
^{1}H NMR comparison

PNB2 from GIII

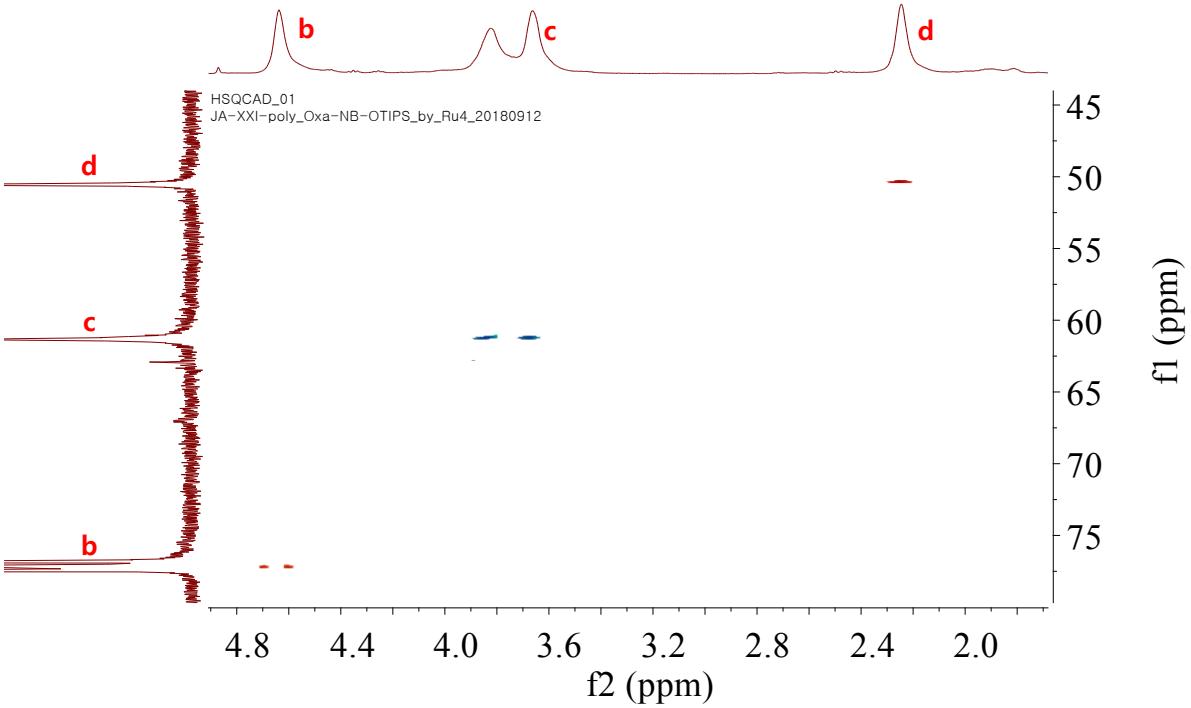
PNB2 from Ru4



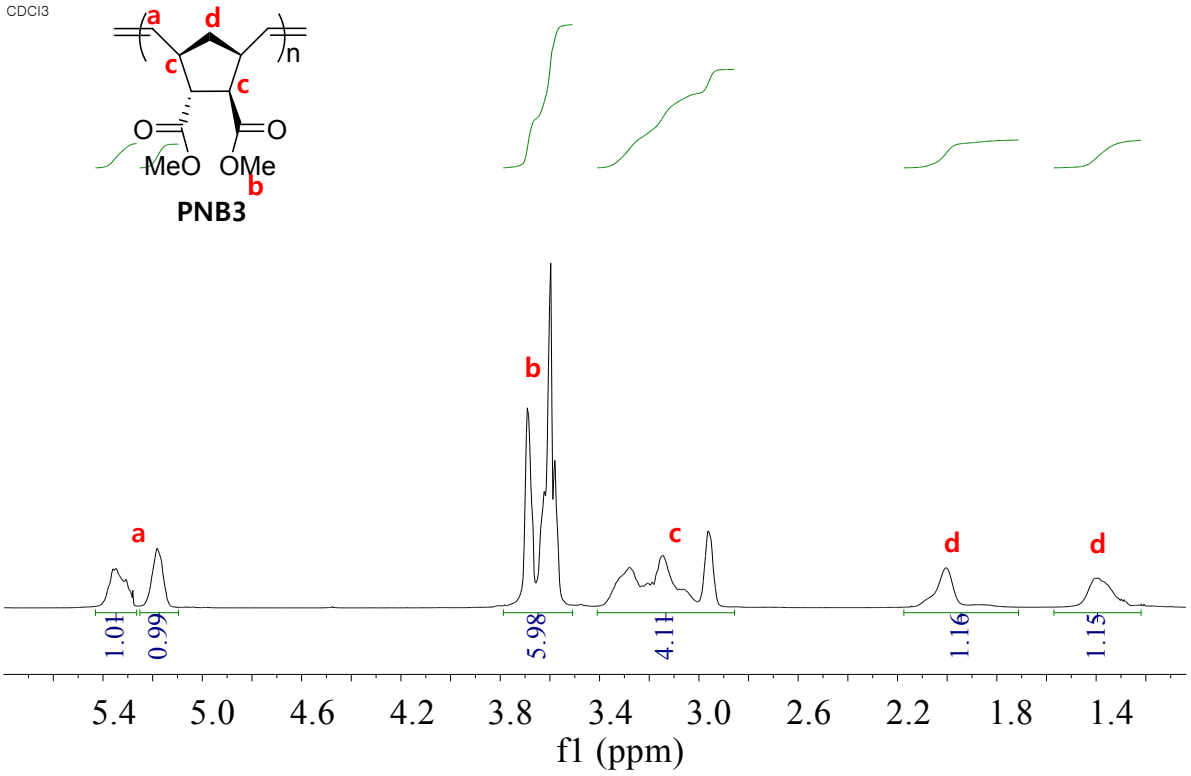
^{13}C NMR spectrum of PNB2 in $CDCl_3$ at RT



HSQC NMR spectrum of PNB2 from Ru4

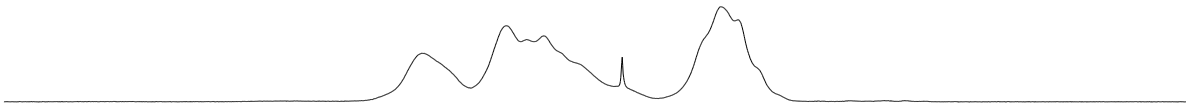


^{1}H NMR spectrum of PNB3 in $CDCl_3$ at RT

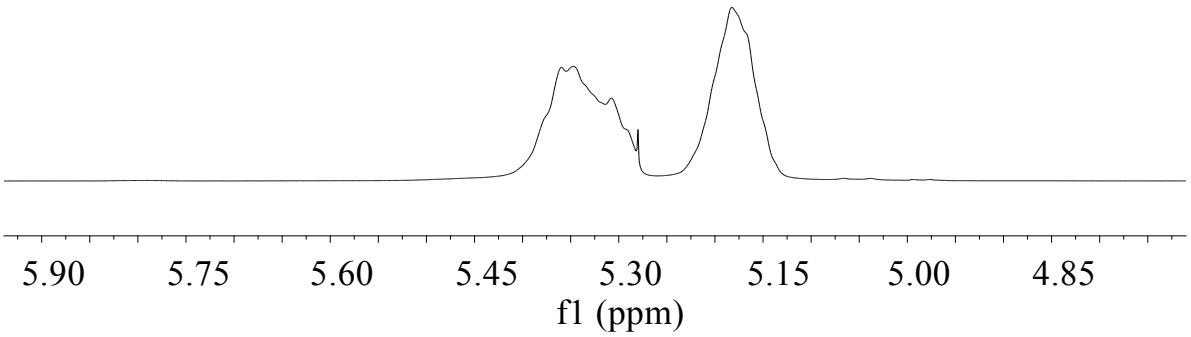


^{1}H NMR comparison

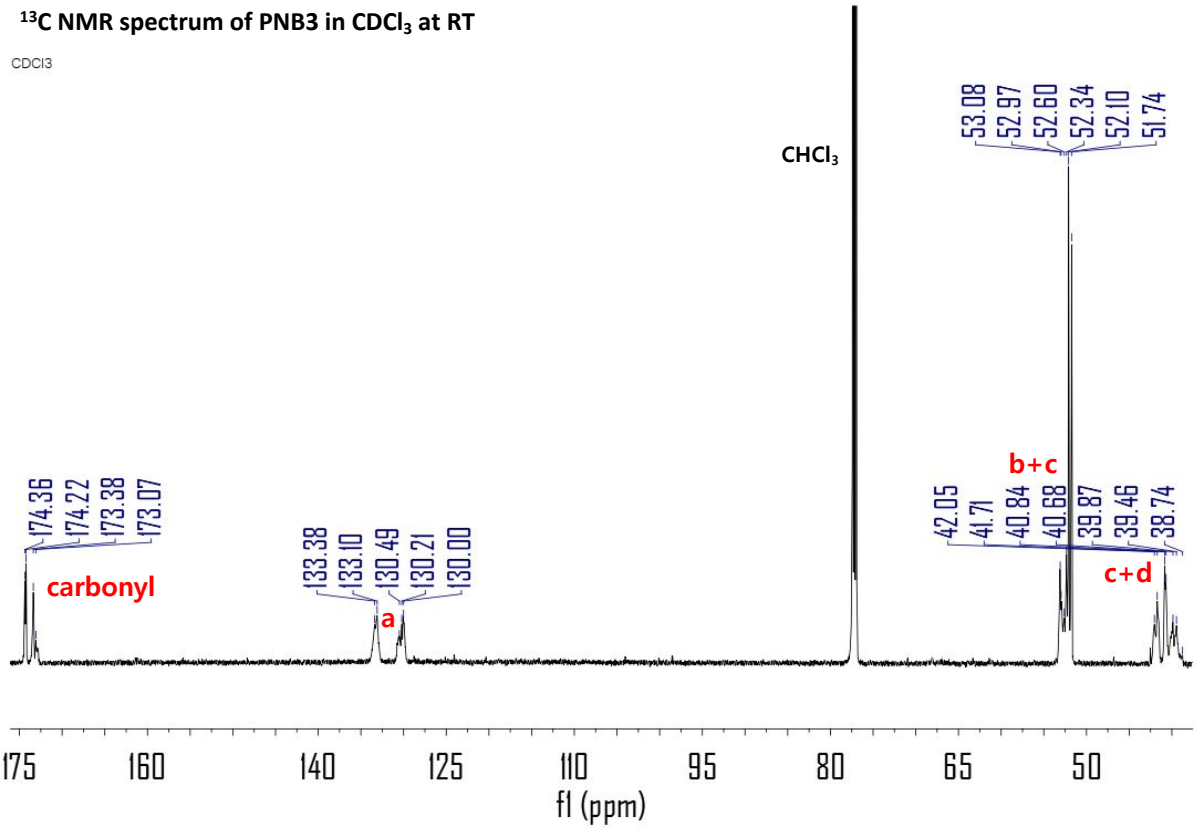
PNB3 from GIII



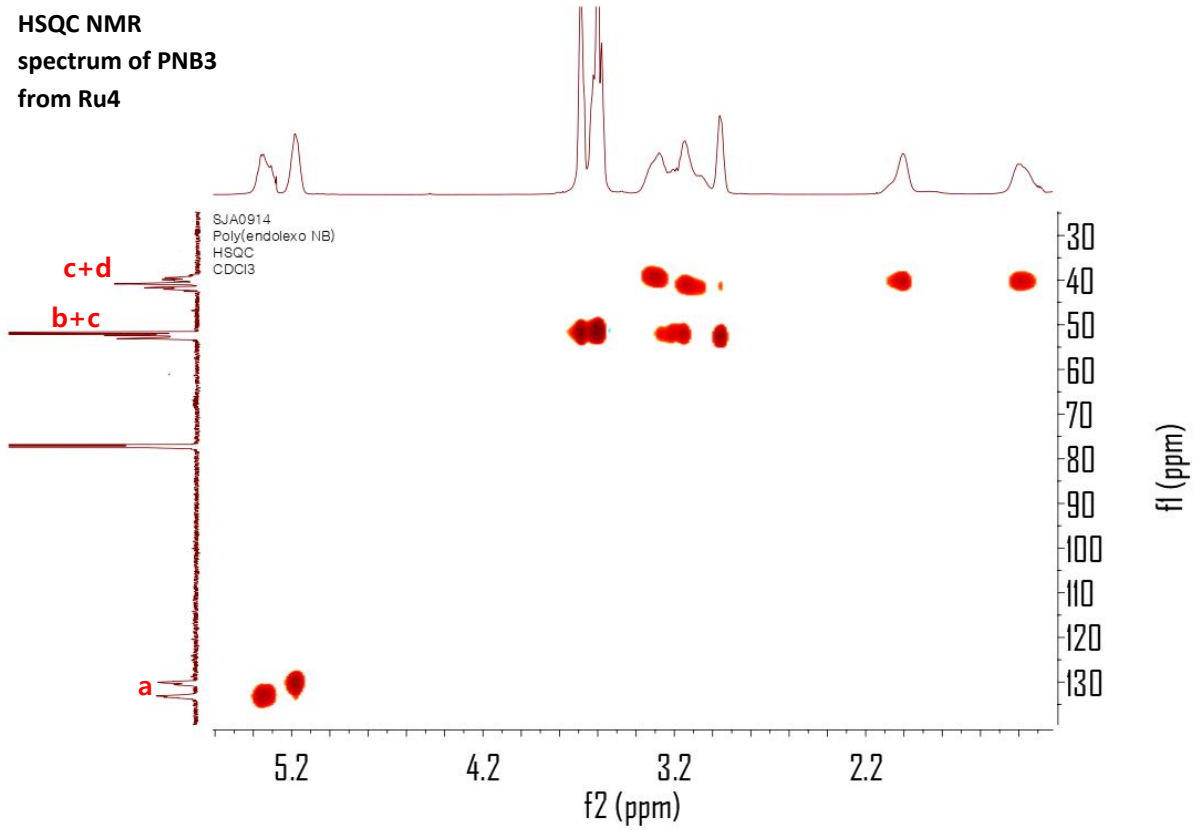
PNB3 from Ru4

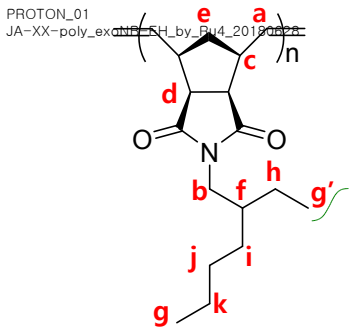


^{13}C NMR spectrum of PNB3 in $CDCl_3$ at RT



HSQC NMR spectrum of PNB3 from Ru4

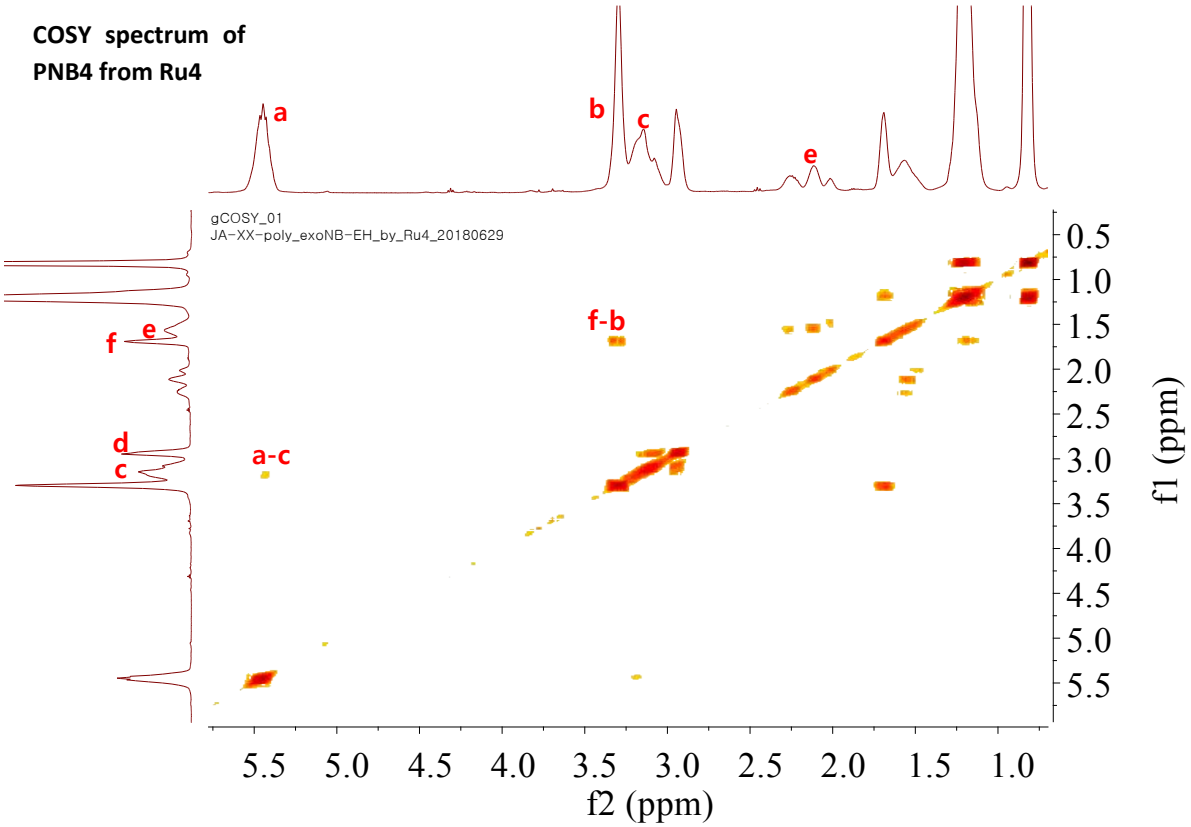




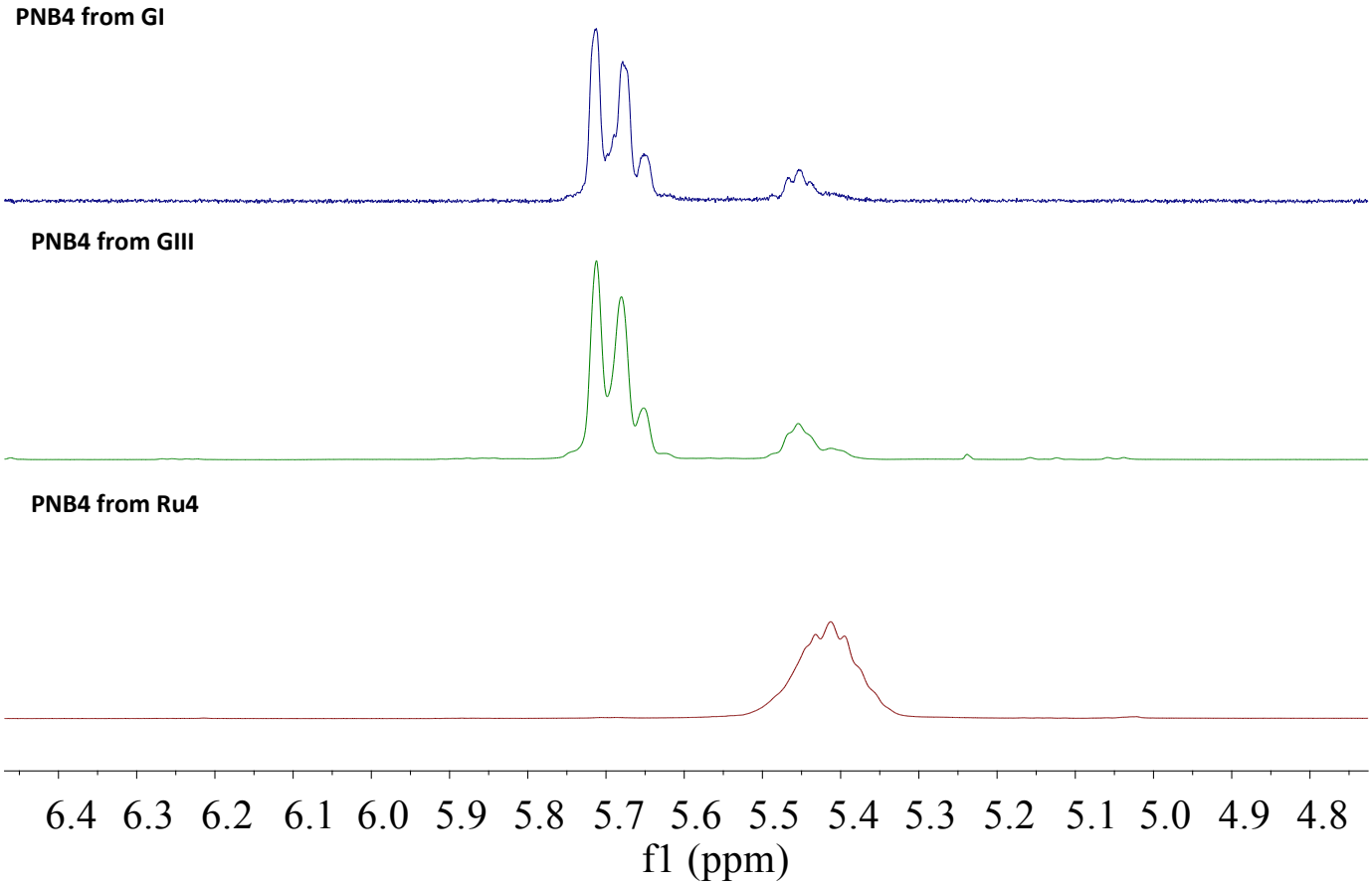
PNB4

^{1}H NMR spectrum of PNB4 in $CDCl_3$ at RT

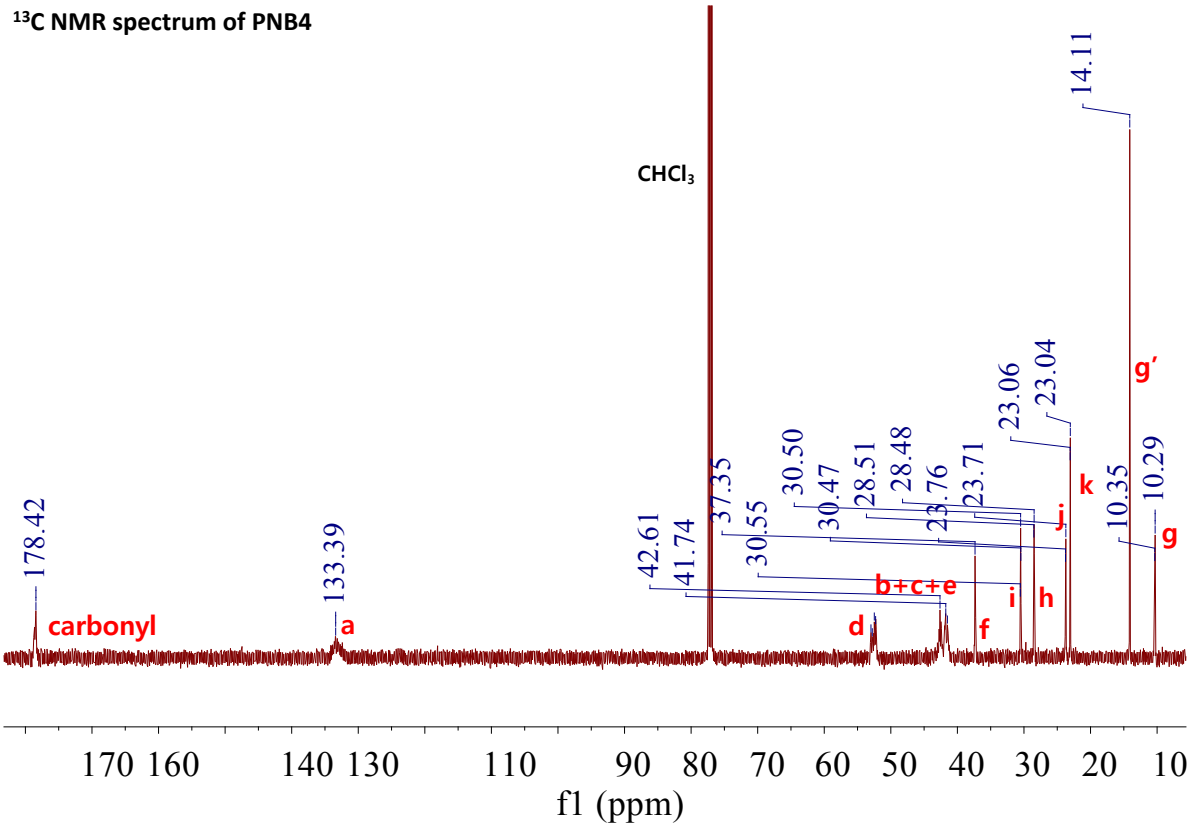
COSY spectrum of PNB4 from Ru4



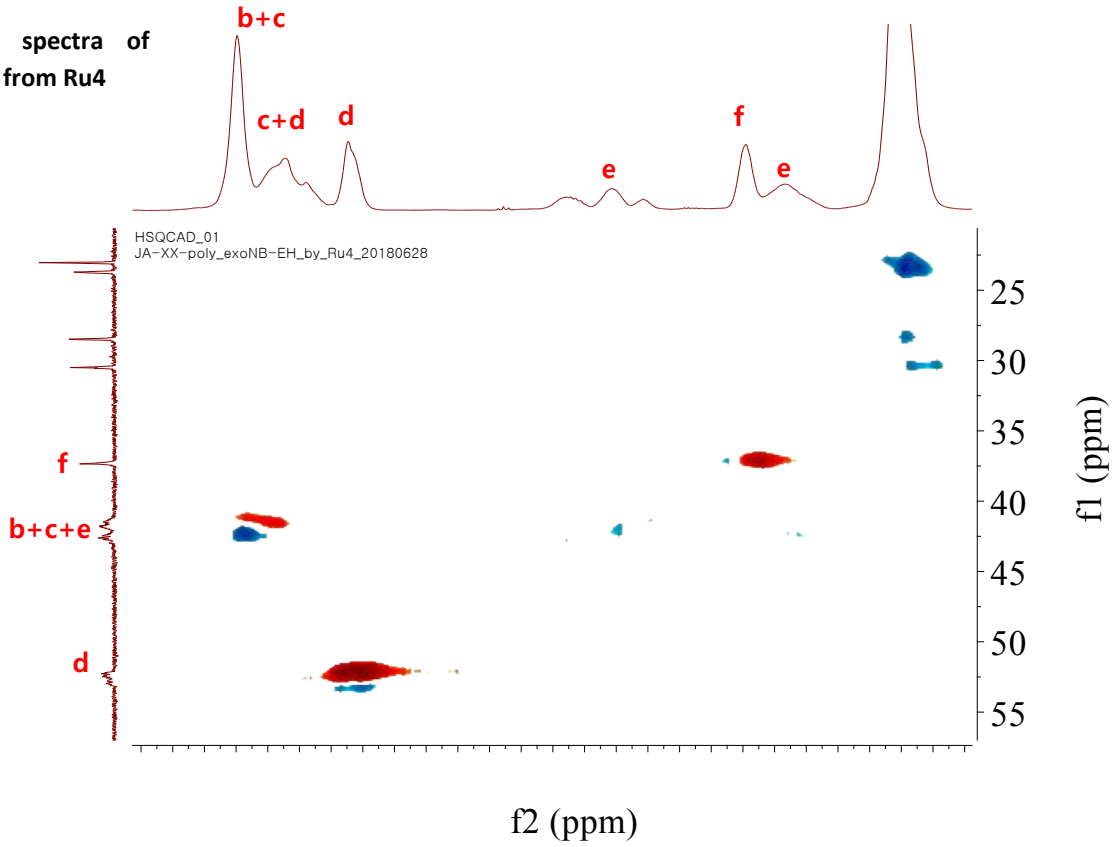
^{1}H NMR comparison



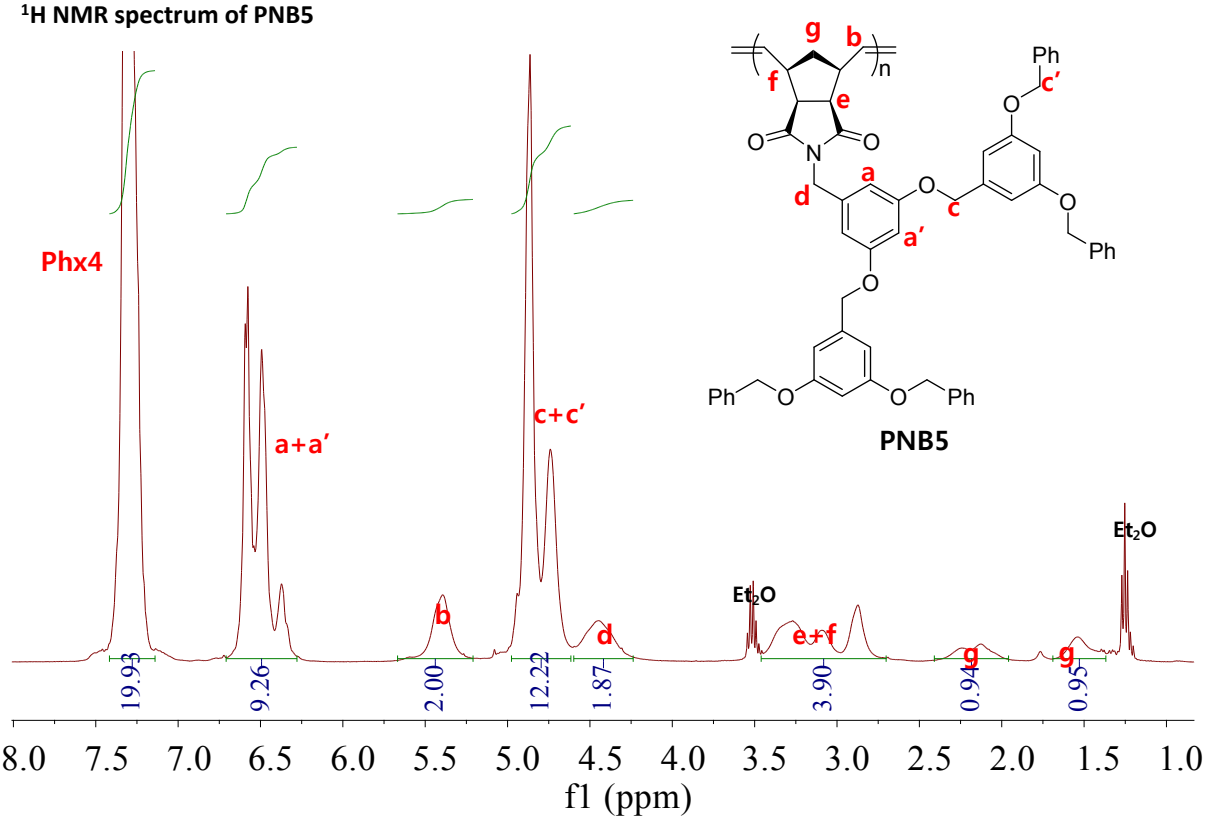
^{13}C NMR spectrum of PNB4



HSQC spectra of PNB4 from Ru4

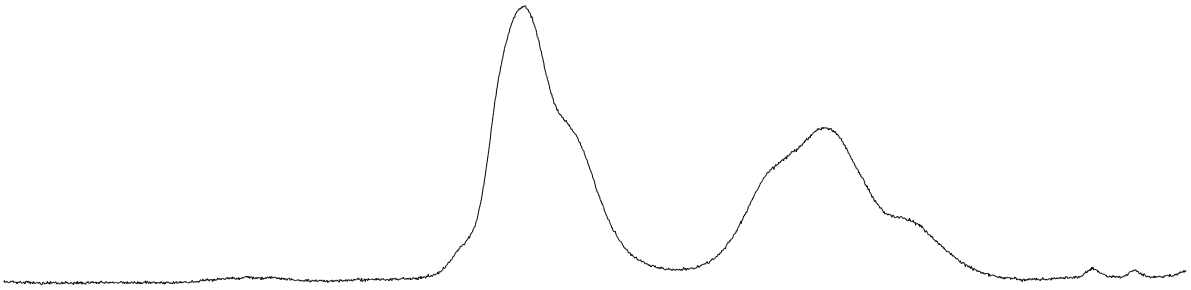


^{1}H NMR spectrum of PNB5

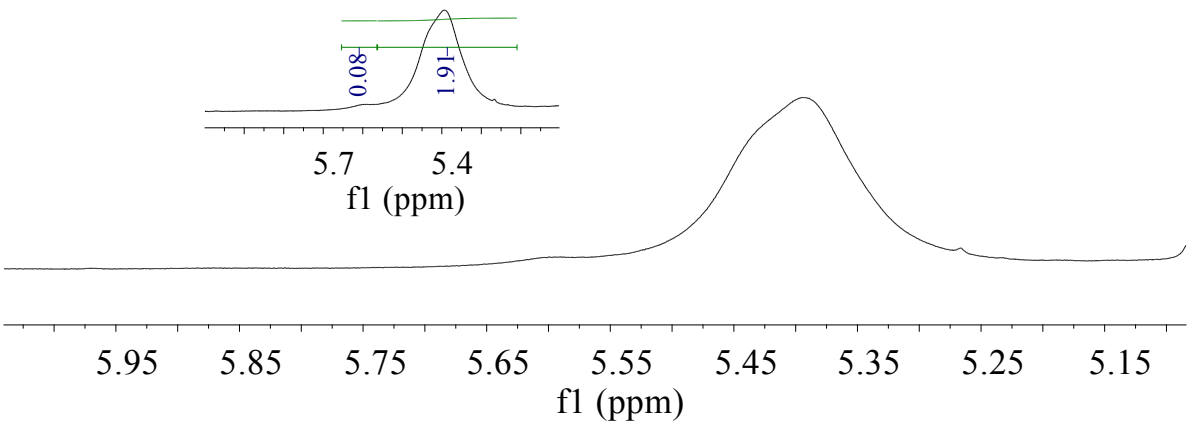


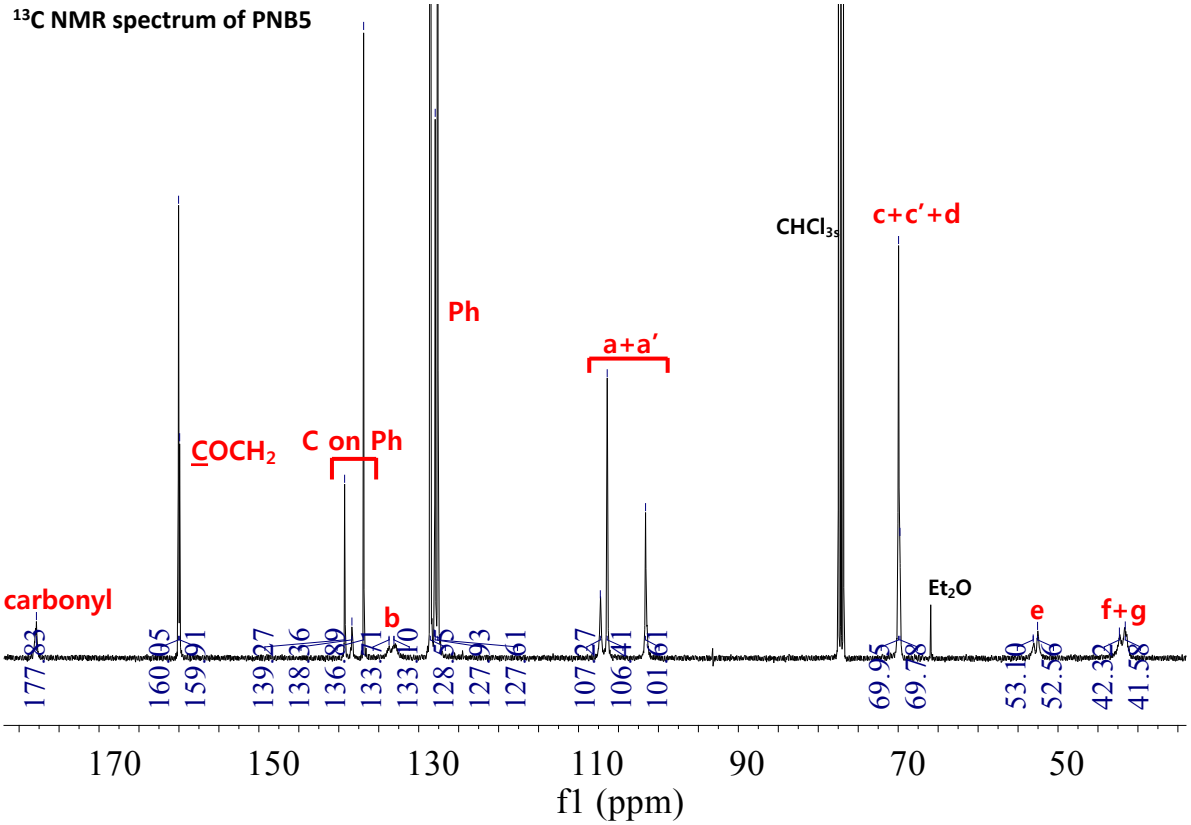
^{1}H NMR comparison

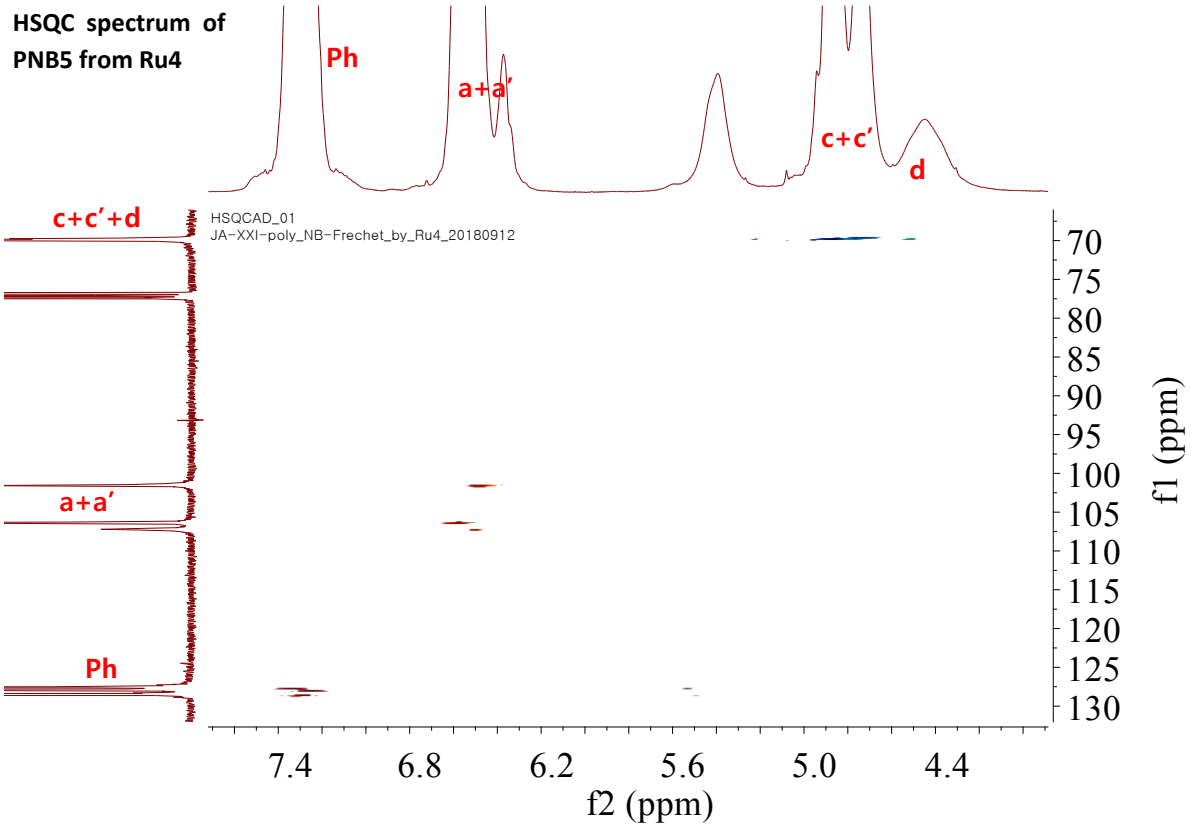
PNB5 from GIII



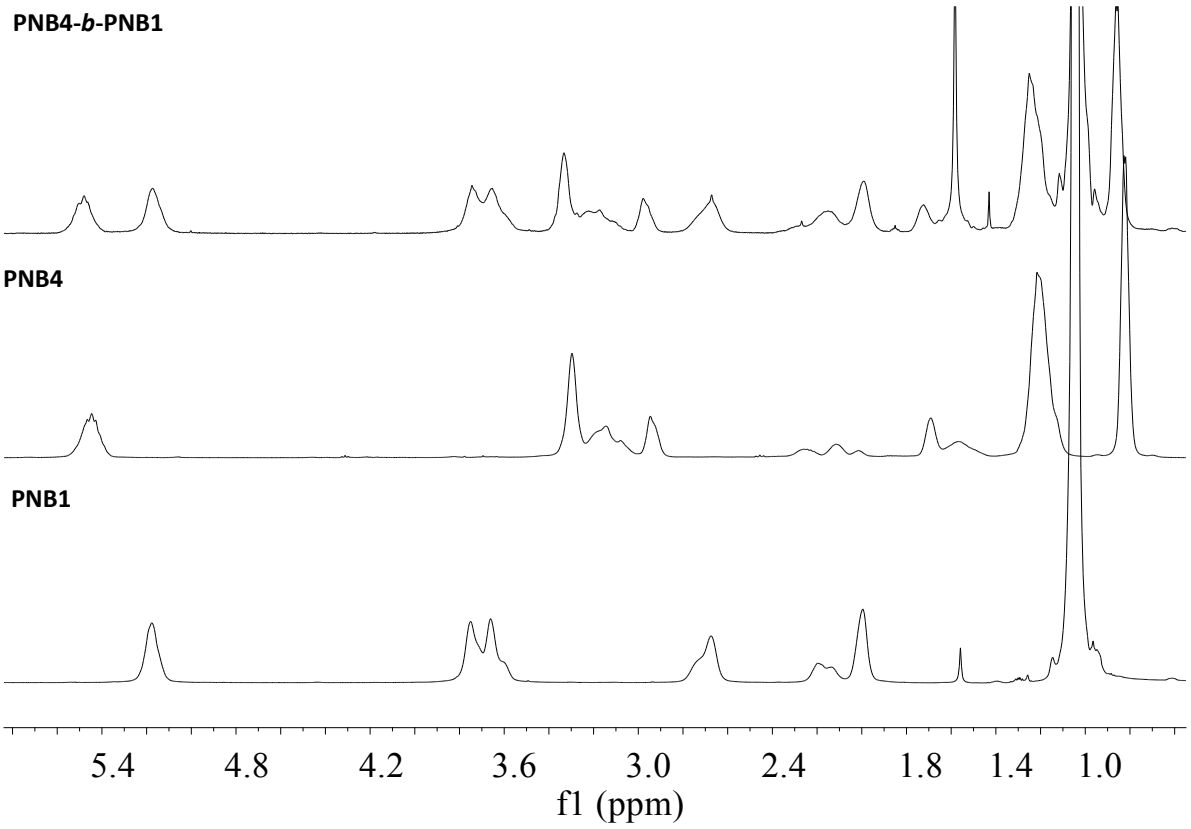
PNB5 from Ru4

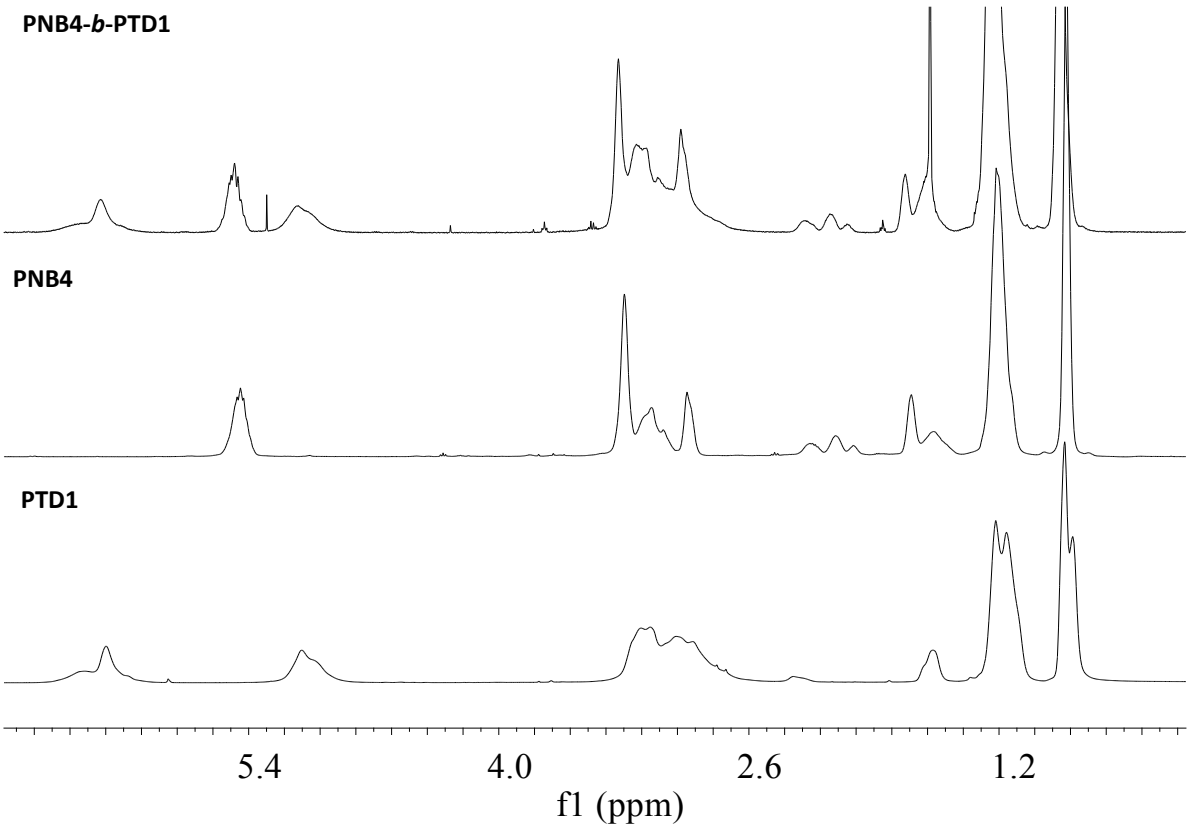



13C NMR spectrum of PNB5
carbonyl
COCH2
C on Ph
b
Ph
a+a′
CHCl3
c+c′+d
Et2O
e
f+g
177.83
160.05
159.91
139.27
138.36
136.89
133.71
133.10
128.55
127.93
127.61
107.27
106.41
101.61
69.95
69.78
53.10
52.56
42.32
41.58
170
150
130
110
90
70
50
f1 (ppm)


HSQC spectrum of PNB5 from Ru4
Ph
a+a′
c+c′
d
c+c′+d
a+a′
Ph
HSQCAD_01
JA-XXI-poly_NB-Frechet_by_Ru4_20180912
70
75
80
85
90
95
100
105
110
115
120
125
130
f1 (ppm)
7.4
6.8
6.2
5.6
5.0
4.4
f2 (ppm)

^{1}H NMR spectra of diblock copolymers





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